# JOURNAL OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS

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# CONTENTS.


| | PAGE |
|---|---|
| One Hundred and Seventy-second General Meeting | 1 |
| **Temperature Measurements in Oil Wells.** M. Schlumberger, H. G. Doll and A. A. Perebinossoff | 1 |
| **A Method of Testing Reflection Seismographs.** J. H. Jones, Ph.D., D.Sc. | 26 |
| **The Use of Reversed Refraction Arcs in Seismic Surveying.** R. Davies, M.Sc. | 31 |
| **Exploration by the Reflection Seismograph in the Gulf Coast of Texas and Louisiana.** E. E. Rosaire | 40 |
| Trinidad Branch. Sixth Annual Dinner | 57 |
| Mr. G. Sell | 60 |
| One Hundred and Seventy-fourth General Meeting | 61 |
| **Some Problems of Modern High-Duty Aero Engines and their Fuels.** F. R. Banks | 63 |
| **Organization of Research in the Petroleum Industry.** Ir. J. H. Vermeulen | 179 |
| **Research and Development Activities in the Standard Oil Company (New Jersey) Interests.** W. C. Asbury and David A. Shepard | 192 |
| One Hundred and Seventy-third General Meeting | 197 |
| **Remarks on Research.** Ir. G. D. Boerlage | 207 |
| **The Desulphurization of Oils.** C. M. Cawley, Ph.D., M.Sc. | 209 |
| **A Table of Specific Gravity Correction Factors for Petroleum Oils.** E. S. L. Beale, M.A., F.Inst.P. | 213 |
| **The Aniline Points of Hydrocarbons.** E. B. Evans, Ph.D., M.Sc., A.I.C. | 220 |
| **The Principles of Solvent Dewaxing.** M. Ba Thi, B.Sc., L. C. Strang, Ph.D., T. G. Hunter, B.Sc., A.R.T.C., A.I.C., and A. W. Nash, M.Sc., F.C.S., M.I.Mech.E. | 226 |
| **Physical and Chemical Constants of Gas Oils with Different Cetene Numbers.** D. J. W. Kreulen | 253 |
| **A Failure of the Standard Method of Estimating Bituminous Content when applied to Limestone.** A. A. Ashworth, M.A. | 266 |
| Roumanian Branch. Tenth Annual Dinner | 270 |
| Annual Reports of the Council and Branches | 275 |
| Twenty-fourth Annual General Meeting | 299 |
| **Extended Vapour-Pressure Chart for Hydrocarbons and Petroleum Products.** E. S. L. Beale, M.A., F.Inst.P. | 311 |
| **The Design and Analysis of Fractionating Columns for Complex Mixtures.** P. Docksey, B.A. | 316 |
| **The Lubrication of Journal Bearings in Oxidizing Conditions.** C. Jakeman and A. Fogg, M.Sc. | 350 |
| Obituary. Carlos Bernard McKeever | 367 |
| Obituary. Theodore Spencer | 368 |
| One Hundred and Seventy-sixth General Meeting | 369 |
| **Geological Aspects of Deep Drilling Problems.** W. E. V. Abraham, A.R.C.Sc.I., B.Sc. | 378 |
| **Preparation and Control of Mud Fluid for Pressure Drilling Conditions.** J. T. Evans | 391 |
| **Drilling of a Deep Pressure Test in India.** G. F. Wilson, B.Sc. | 401 |
| **Notes on Deep Wells Drilled in Iran.** G. W. Colvill | 408 |

PAGE

**Deep Well Drilling.** Discussion by Roumanian Branch . . . . . 412

**A New Type of Threaded Connection for Oil Well Casing.** W. M. Frame . 422

Obituary. Thomas Richard Henry Garrett, O.B.E., M.A. . . . . 426

**The Viscometer with Suspended Level. (The Elimination of the Influence of Surface Tension by the Suspended Spheric Level.)** Prof. Dr. L. Ubbelohde . 427

**The Coefficient of Static Friction of Different Lubricating Oils measured with the "Redgrove" Apparatus.** D. J. W. Kreulen . . . . . 452

**Hydrogenation of Some Benzene Hydrocarbons under High Pressure.** M. K. Diakova, A. V. Losovoy, and T. G. Stepantzeva . . . . . 459

Correspondence. Anomalous Results for Soluble Bitumen of Natural Rock Asphalts . . . . . 466

**The Present State of our Knowledge on the Origin of Petroleum.** C. D. Nenitzescu . . . . . 469

**The Activity of Oxygen towards Hydrocarbon Mixtures with a High Molecular Weight.** H. I. Waterman, J. J. Leendertse and E. C. H. Palm . . . 483

**The Adsorption of Bitumens by Road Aggregates.** J. R. Ramchandani, M.Sc. (Eng.), D.I.C., B.E. . . . . 491

**Alcohol Motor Fuels.** A. R. Ogston . . . . . 506

**Forestry in Relation to the Petroleum Industry.** R. L. Brooks, Dipl.For.(Edin.) 524

**The Microscopical Examination of Crude Petroleum.** J. McConnell Sanders, F.I.C., F.C.S. . . . . 525

Obituary. William Hardy Manfield . . . . . 574

**Research in Relation to the Motor Vehicle—Fuels and Lubricants.** F. H. Garner, Ph.D., F.I.C. . . . . 575

**The Determination of the Ignitability of Diesel Oils on a Laboratory Scale.** R. Heinze and M. Marder . . . . . 602

**Petroleum Wax: Determination, Analysis, and Conclusions about Its Composition.** D. S. McKittrick, H. J. Henriques, and H. I. Wolff . . . 616

Correspondence: Aniline Points of Hydrocarbons; Anomalous Results for Soluble Bitumen of Natural Rock Asphalts . . . . . 642

**Synthetic Products from Petroleum.** G. Egloff, Ph.D., M.A. . . . . 645

**The Chemical Constituents of Paraffin-Base Lubricating Oils.** J. Müller and E. Neyman-Pilat . . . . . 669

**The Formation of Organo-Metallic Alkyl Derivatives of Aluminium during the Polymerization of Ethylene.** F. C. Hall, Ph.D., A.I.C., and A. W. Nash, M.Sc., M.I.Mech.E., F.C.S., M.I.Chem.E. . . . . 679

Nineteenth Annual Dinner . . . . . 688

Correspondence: Determination of the Ignitability of Diesel Oils on a Laboratory Scale . . . . . 703

Obituary. Paul de Chambrier . . . . . 705

**The Principles of Solvent Dewaxing. Part II. Equilibria and Computations for Double Solvent Systems.** M. Ba Thi, B.Sc., A.I.C., T. G. Hunter, Ph.D., A.R.T.C., A.I.C., and A. W. Nash, M.Sc., M.I.Chem.E., M.I.Mech.E. . . 707

**Dewaxing with Heavy Solvents.** B. Engel . . . . . 723

**The Influence of Certain Substances on the Separation of Paraffin Wax from Oil in a Dewaxing Process.** E. C. H. Kolvoort, F. R. Moser, and C. G. Verver . 734

**Methyl Normal-Butyl Ketone as a Dewaxing Solvent.** O. S. Pokorny and R. K. Stratford . . . . . 746

One Hundred and Seventy-seventh General Meeting . . . . . 751

**Marine Drilling.** A. J. Ruthven-Murray, M.A., B.Sc., F.G.S. . . . . 760

Author Index . . . . . 771

Subject Index . . . . . 775

PAGE
412
422
426
427
452
459
466
469
483
491
506
524
525
574
575
602
616
642
645
669
679
688
703
705
707
723
734
746
751
760
771
775

SIR JOHN CADMAN, G.C.M.G., D.Sc., Hon. LL.D.
*President*, 1935–1937.

*From the painting by John A.A. BERRIE, R.C.A.*



UNIV. OF MICH.

# THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE One Hundred and Seventy-second General Meeting of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, London, on Tuesday, November 10th, 1936. The Chair was occupied by Professor V. C. ILLING (Member of Council).

PROFESSOR V. C. ILLING, in opening the meeting, said that the President, Sir John Cadman, had asked him to express his great regret at being unable to attend the meeting, as he had been called away to the north. Personally he was very sorry that Sir John was not able to be present, for on this occasion there were present at the meeting not only members of the Institution of Petroleum Technologists, but also members of the Institution of Mining and Metallurgy and of the Geological Society. He was glad to have the support on the platform of the President of the Geological Society, and Professor Cullis, Vice-President of the Institution of Mining and Metallurgy, was also present. He took it that their presence was an indication of the widespread interest of the subjects dealt with in the papers to be presented that evening.

The following paper was then presented by Mr. A. A. Perebinossoff, after a few words of introduction by Mr. M. Schlumberger:

## TEMPERATURE MEASUREMENTS IN OIL WELLS.

By M. SCHLUMBERGER,* H. G. DOLL* and A. A. PEREBINOSSOFF.*

SYNOPSIS.

Continuous temperature measurements in oil wells can now be made with an extremely sensitive recording thermometer. They can be applied to a great number of oil-field problems, both in wells in thermal equilibrium and in wells in thermal evolution, and also both in open and in cased holes.

The data on geothermal gradients and their variations interest both the regional and local geologist. Knowledge of subsurface temperatures can aid the technologist in problems related to mud and cementing.

Temperature measurements can yield valuable corroborative data on the sequence of formations in a well, the main data always preferably being given by electrical logging. They can be applied to location of water, oil- or gas-sands, both in drilling and in already tested or produced wells. They are invaluable for checking the results of a cementing operation.

The paper presents the principles of the major thermometric techniques, and illustrates them with some practical examples. In conclusion, attention is drawn to the time and care that may sometimes be required for optimum results, but practice has already proven that the best local operating conditions are very soon determined in most regions, thanks to the spirit of co-operation existing between the surveyor and the local technologists.

* Société de Prospection Electrique, Paris.

## Introduction.

Recent years have shown a most striking development in what may be termed the more scientific study of wells, and much new, or more complete and reliable information is thus available to the oil-field technologist. Accurate and complete deviation surveys are now quite common, likewise bottom-hole pressure measurements. The strike of formations can be determined in situ, and their nature and contents are studied by means of the process termed " electrical logging."

Another physical parameter available inside wells is temperature. Its more than probable practical value has never been doubted, one might say, ever since wells were first drilled. But its extensive measurement was hampered by the lack of a suitable and practical instrument, and, consequently, of an adequate operating technique. " Single-shot " bottom-hole temperature measurements were, of course, always possible, but the maximum amount of data can only be had by tracing a continuous temperature log over at least a certain portion of the hole. As a practical additional condition, this log must be obtained in sufficiently short a time.

Such an instrument has now been evolved, and has been in actual field use for the last few years. Results are more than encouraging, and the main object of this paper is to explain the principles of the techniques applied to the numerous problems that it can solve, and to present some theoretical, as well as practical, examples.

## General Principles.

The instrument in question is based on the well-known phenomenon of the variation of the electrical resistance of a conductor in function of its temperature. The Wheatstone bridge principle can be used, and it will readily be understood that a potential difference measurement can be substituted for that of the resistance, and consequently of the temperature. Just as for electrical logging, the potentiometer can be connected to a suitable recorder, and the continuous temperature log is thus obtained at the well.

The principle is simple, but considerable practical difficulties had to be overcome. The instrument must be capable of withstanding the high pressures encountered in deep wells. Electrical insulation must remain perfect. But, at the same time, the sensitive part of the circuit must take the temperature of its surrounding medium in as short a time as possible. The present type of instrument has a diameter that can allow it to be run through all but the very smallest and exceptional sizes of drill-pipe and tubing. Its accuracy is 0·1° C. (or 0·2° F.), and the " time-constant " is such that continuous logs can be traced at the satisfactory speed of about 15 cm. per second, or roughly 2000 ft. per hour, without any appreciable lag.

The instrument is run inside the well, and is in contact with the fluid (usually drilling mud) contained therein. It therefore measures the temperature of this fluid, and not the temperature of the formations or other substances (for instance, casing, cement) surrounding the said fluid. It is scarcely necessary to add that these surroundings will, of course, exert a more or less preponderant action on the temperature of the fluid.

The above remark may serve to divide temperature measurements in wells into two main sections:

(*a*) The fluid in the well is in thermal equilibrium with its surroundings;

(*b*) The fluid in the well is not in thermal equilibrium with its surroundings. The temperature log will record the exchange of heat occurring between the two, and, since the exchange depends on the thermic properties of the latter, much useful information can be obtained thereon by this method.

Finally, it must be added that these two main subdivisions seemingly apply to the case of a well filled with one single fluid. Temperature measurements can, of course, just as well be used when the exchange between the surroundings and the inside of the well is not merely limited to heat; actual material flows of oil, gas, or water into the well can also be revealed by an appropriate temperature run.

## Study of Wells in Thermal Equilibrium.

The information obtained from the study of wells in thermal equilibrium comes down to ascertaining the geothermal gradient of the formations, and, in particular, to determining the natural sub-surface temperature at any given point.

A certain time will have to elapse before such information can be available, not so much because the fluid itself in the hole must attain the temperature of the surroundings, but because these latter have also usually been influenced by the previous drilling or producing history of the well, and must therefore return to their normal state of thermal equilibrium. In drilling wells, the cooling (or sometimes, warming) effect of the circulating fluid will naturally depend on the time during which this circulation has lasted. In producing wells, gas expansion can be very important, not to mention the movements of other fluids, such as oil or water.

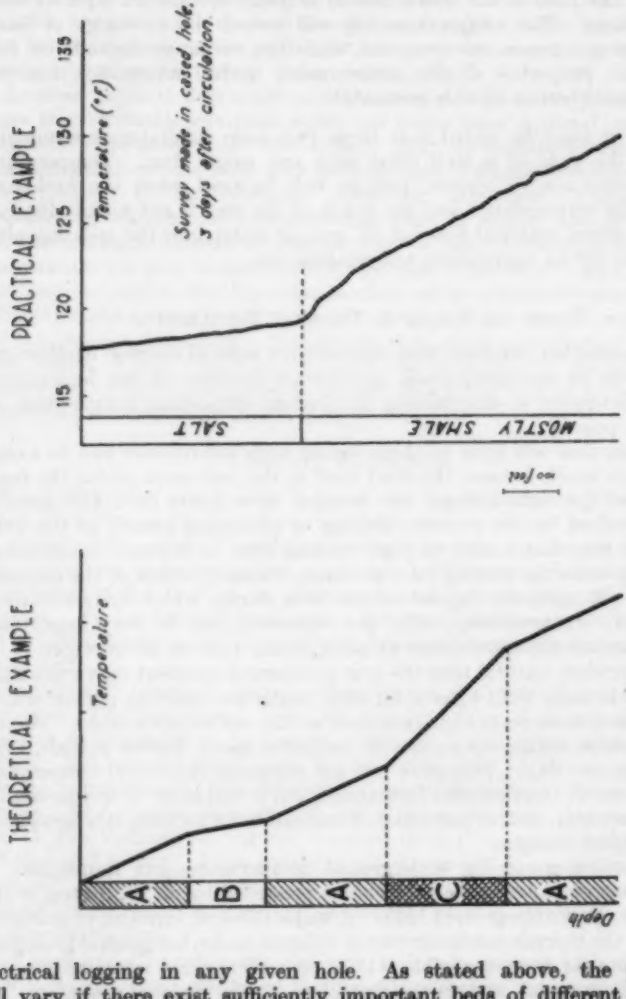
It is therefore natural that the true geothermal gradient curve can only be logged in such wells after a far from negligible standing period, which may in some cases be as high as several weeks, not to say months. Nevertheless, useful results may often be had after much shorter periods, even as short as one day. The curve will not represent the actual temperature of the thermally undisturbed formations, but it will more or less be similar to the true curve, and, in particular, it can suffice for locating stratigraphical or lithological changes.

The factors governing underground temperatures are numerous. A comprehensive paper in the subject was presented by M. W. Strong at the World Petroleum Congress of 1933. A major cause of variation of gradients resides in the thermic conductivities of different rocks, but general geological features are far from negligible. Data on underground temperatures can thus be most useful, and, in the first place, to the regional geologists. In this respect, we also recall the numerous articles published by C. E. van Orstrand in the United States of America.

The data will also interest the more local geologist. The above-mentioned authors have explained what relation may exist between tem-

perature and structural conditions: anticlines, probable depths of underlying major horizons, faults, and so on. There is therefore no need to enlarge upon this subject in the present paper.

Still more locally, temperature measurements may often supplement




VARIATION OF THE GEOTHERMAL GRADIENT IN FUNCTION OF THERMAL CONDUCTIVITY.

Fig. 1.

electrical logging in any given hole. As stated above, the gradient will vary if there exist sufficiently important beds of different thermal conductivities. Without going into details (influence of anisotropy, etc.) it is known that the thermal conductivity of different rocks varies over quite considerable a range. Fig. 1 shows a theoretical diagram on the left and a practical one on the right. In this case, the example is particu-

larly interesting, since the base of the salt was determined exactly in a cased hole, and only three days after circulation had been stopped.

Finally, the field engineer can derive much useful information from temperature surveys for problems connected with mud technique, cementing and even corrosion. Very deep wells give rise to very special conditions for all such problems, and it might be recalled here that it has been stated that the relative ease with which the record well McElroy 103 was able to reach such depths may have been partly due to the low temperatures encountered therein (only 182° F. at 12,786 ft.). The knowledge of underground temperature conditions may serve as basic data for laboratory experiments, resulting, for instance, in determining the best treatment of the mud and whether addition of ice is necessary or not for the cementing job.

For such data, it is not always necessary to wait for the well to reach its thermal equilibrium, and successive temperature surveys may likewise give much valuable information. This sentence may thus serve as transition to the next, and most important, chapter of this paper.

## Study of Wells in Thermal Evolution.

The principle of the phenomenon may be explained as follows (refer to Fig. 2). Let us suppose a well 5000 ft. deep, and, neglecting any perturbing action, let us also suppose that the normal geothermal gradient is a straight line running from 60° F. at surface to 140° F. at bottom (curve 1). The circulating fluid filling the entire hole may have a constant temperature, for instance, of 85° F. (curve 2), but, much more likely, it will be somewhat cooler near the surface. Let us suppose that immediately after circulation, the temperature of the fluid is represented by curve 3, whereas curve 1 represents the temperature of the fluid after thermal equilibrium has been reached.

In the intermediate stage, the fluid above point *X* will be cooling off, and the fluid below this point will be warming up, so that if a temperature run is made, and if the formations are supposed to act identically as regards thermal effect, the intermediate curve 4 will be found to lie between curves 1 and 3.

But, evidently, the warming and cooling effects will be far from the same opposite different formations, and, for instance, water-sands, having a high thermal conductivity, will tend to reach their thermal equilibrium quicker than the surrounding shales, for instance. This is chiefly due to the convection currents circulating therein, which are probably quite important, as stated by one of the above-mentioned authorities at a Meeting of this Institution held in June 1935. Such sand bodies will therefore show up on the intermediate temperature logs, as seen on curve 5.

An important remark may be made here concerning convection currents existing within water-sands, and other porous layers in general. Their action will exert itself continuously during the entire actual circulation period, thus preventing any appreciable alteration of the temperature of the porous layers themselves, even in the immediate vicinity of the hole. This because the convection currents will at once disperse into the mass any calories (or frigories) taken from the circulating fluid. Practically,

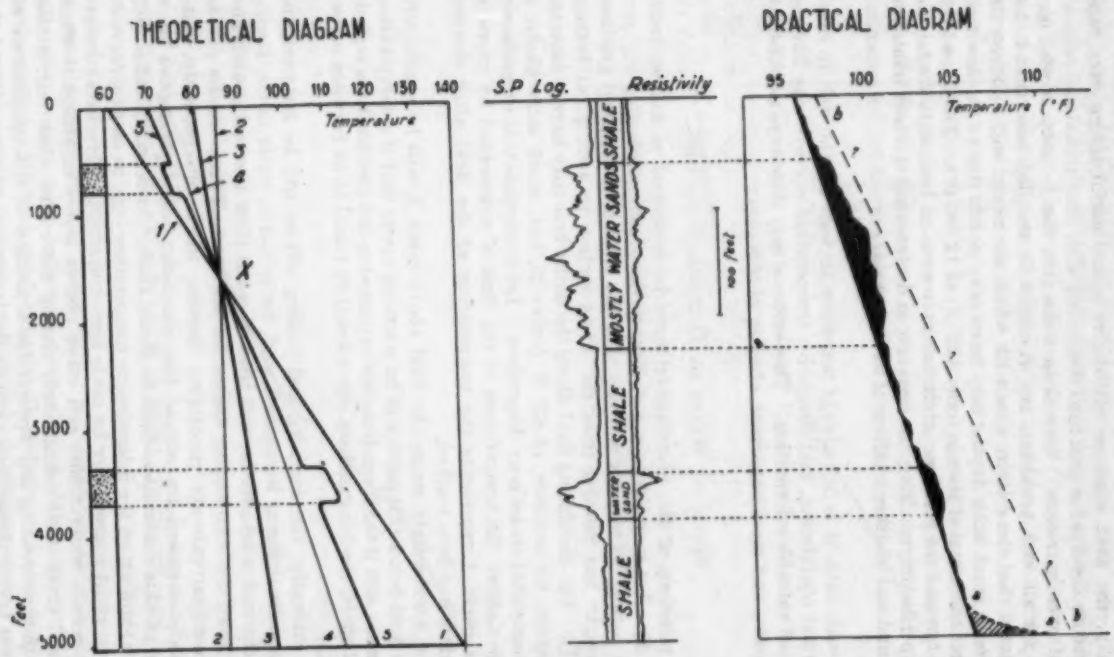



FIG. 2.

VARIATION OF THE TEMPERATURE OF THE FLUID IN THE HOLE AFTER CIRCULATION (WATER-SANDS).

the result will always be that shown on curve 5, but it has been thought advisable to stress on this explanation of the temperature stability of porous layers, even after circulation, and on their resulting very rapid influence on the fluid within the hole.

It is scarcely necessary to add that the "pivotal" point *X* on Fig. 2 has a position which varies from well to well and depends on the local conditions. In some cases it can lie either above or below the portion surveyed. It is likewise scarcely necessary to add that the maximum thermal differential effect opposite sands (and other formations) in a given well is obtained at a certain given time after the end of circulation. Experience has proved, however, that one soon determines what time must elapse in order to obtain sufficiently clear results.

## I. Measurements in Open Hole.

(*a*) *Corroborative Formational Evidence.* As a direct application of the above principle, the right-hand portion of Fig. 2 gives an actual example of the corroborating or supplementary evidence obtained in a drilling well, by means of the temperature log. The circulating period is automatically given by the normal drilling, and one must merely make the temperature run sufficiently long after stopping circulation as not to risk obtaining a flat curve like No. 3 of the theoretical diagram.

The diagram was obtained a few hours after circulation. For convenience, a "base line," representing the general trend of the temperature, can be drawn, and the space between it and the actual curve blackened in. For this reason, it is always sound policy to make the survey over as long a section as possible. The smallest local variations are thus shown up very clearly. The dotted line *bb* may represent the equilibrium stage, comparable to curve 1 of the theoretical diagram, towards which the well is tending.

It will be noticed that the temperature curve is generally less detailed than the normal electrical log, which has also been represented. This is, of course, quite natural, in view of the damping effect of the mud and the general technique of temperature measurements. It is for this reason that temperature measurements for mere formational evidence cannot replace the electrical log. But they can, and often do, give valuable supplementary information.

Finally, it will be noted that a hatched portion *aa* has been represented at the bottom of the section. This in order to stress the fact that, if this bottom did actually correspond to the bottom of the hole, a noticeable increase of temperature would most probably have been found there. This is probably due, not so much to the heat developed by the drilling action of the bit, but to the fact that the effect of the mud circulation has not yet had time to complete its cooling effect right to the bottom of the hole, and that the temperature there is consequently closer to natural. Almost every single drilling well surveyed to the very bottom shows such increases, and the practical conclusion is that temperature anomalies near bottom should always be interpreted with the utmost care.

(*b*) *Location of Gas- and Oil-sands in Drilling Wells.* Natural convection movements are not the sole factors affecting the temperature of porous

VARIATION OF THE TEMPERATURE OF THE FLUID IN THE HOLE AFTER CIRCULATION (WATER-SANDS).

layers. If the sands are being or have been produced in neighbouring wells, they will be colder than the surrounding formations because of the gas expansion, or perhaps warmer, in the case of water movement. Consequently, gas- or oil-sands, for instance, can show up by negative thermal anomalies, even if they have not been produced in the well being surveyed.

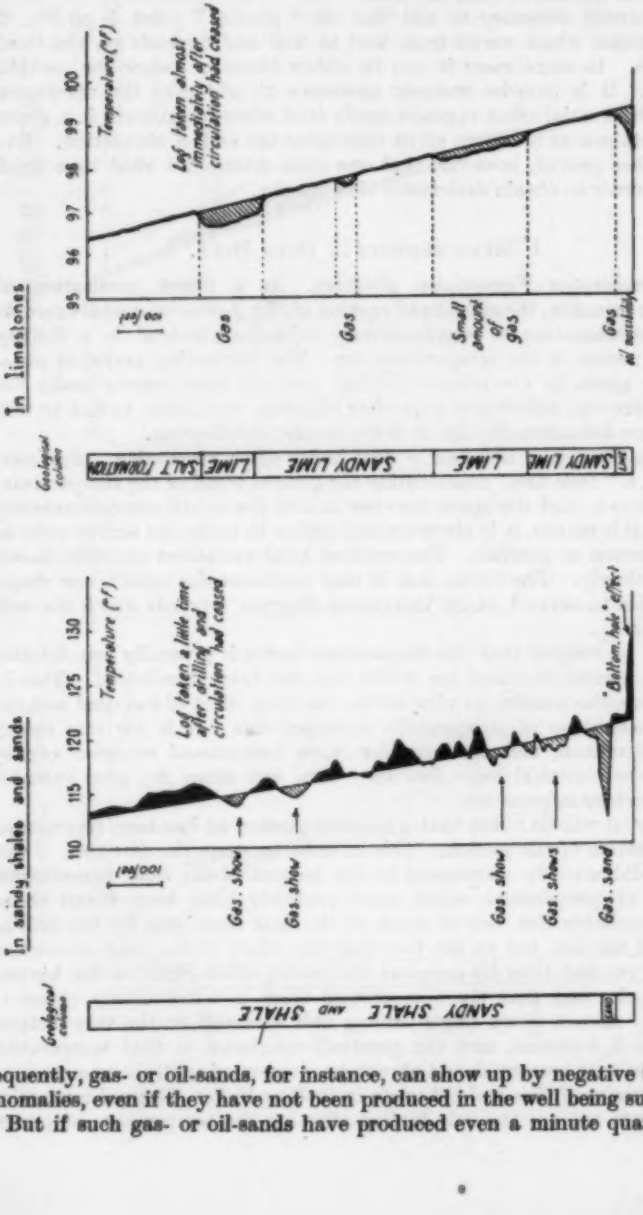



FIG. 3. LOCATION OF GAS (AND OIL) BEARING LAYERS IN DRILLING WELLS.

But if such gas- or oil-sands have produced even a minute quantity of

gas into the well, their location will usually be quite easy. Present theories seem to consider that a certain amount of connate fluid (to wit—gas, with or without oil) will almost always escape into the well when one drills through an oil, or especially a gas-sand, even when the gravity of the mud is well above the danger-value.

Practice bears out this theory, and the left-hand part of Fig. 3 gives an actual example of gas-bearing portions located by this method. The example is particularly interesting in that all the layers, with the exception of the lowest one, are merely sandy, and not pure sand.

The same remark applies to limestone and similar fields, where production is often confined to fissured or porous sections of the formations. Temperature logs are proving most valuable in such fields, and an example is given on the right-hand part of Fig. 3. It will be noticed that the temperature anomaly is extremely small (sometimes less than 1/2° F.), but the accuracy of the instrument allows it to show up unquestionably. It will also be noticed that, in spite of its being at the bottom of the hole (positive temperature anomaly—as explained above), the lowest lime gives the greatest negative effect. This allowed one to suppose that this lime might be productive. Casing was set up at its top, and a test confirmed this interpretation.

(*c*) *Location of Water Flows.* Thermal anomalies will, of course, be much more important inside the well, if the layers are purposely made to produce their flows into the hole. This applies particularly to water flows, either in open-hole or in wells lined with a production string. It is usually easiest to condition the hole by circulating it with a relatively cold mud (quite often just the normal drilling mud), since the water flows are generally warm. In any case, their temperature is often known before conditioning is started, and adequate steps can always be taken to obtain sufficient differentiation. It will be noticed that there is here no call to condition the well with muds of appropriate, and sometimes difficult to attain, salinity, as in the case of water-flow determinations by the well-known and proved salinity methods.

The hole once conditioned, a check run is made to verify this and to obtain a reference curve. The fluid level is then lowered sufficiently to allow the sands to yield up their contents, by any known method (bailing, swabbing, etc.). Further temperature runs are then made, and the procedure is continued until the points of entry are properly located and confirmed.

It is believed unnecessary to discuss this method further, and Fig. 4 gives a simple but typical example obtained on the field.

(*d*) *Location of Gas, Oil (and Water) Flows.* The method just described could theoretically apply equally well to gas- and oil-sand determinations. However, practically, there is a certain attendant danger in lowering the level—risk of blow-outs, etc.

The thermometer is nevertheless able to cope with such cases, by the application of the following principle :—

In all but very shallow drilling wells, the circulation of the mud generally cools the non-porous formations over a certain radius near the well, the porous layers remaining at their approximate natural temperature, because of the presence of convective currents, as explained above when discussing the theoretical diagram of Fig. 2. As such, the porous layers will all show

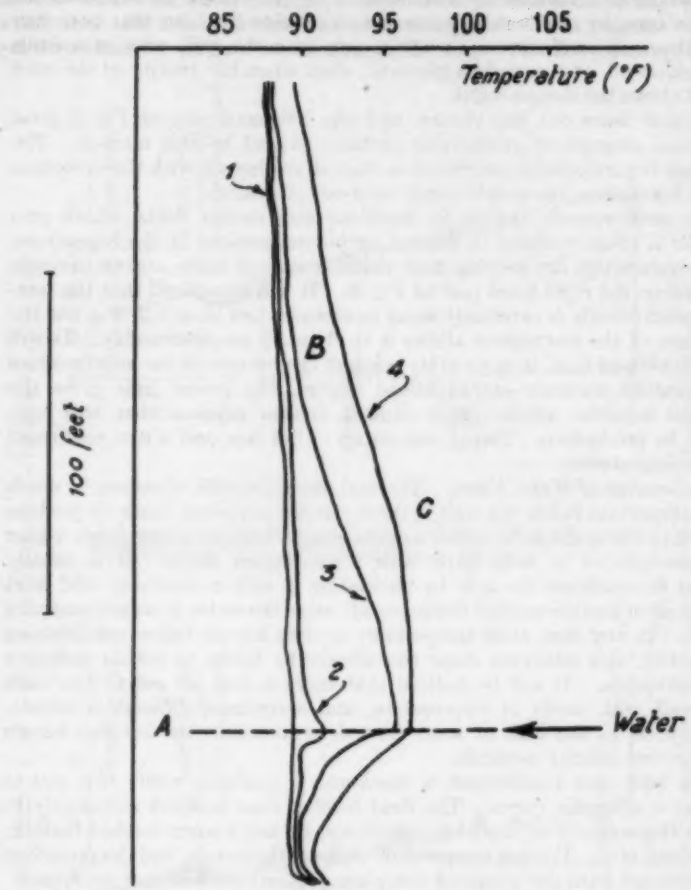



FIG. 4.

LOCATION OF AN ACTUAL WATER FLOW.

Curve 1.—Check-run after circulation and before lowering the level below natural hydrostatic head.

Note slight increase at very bottom—due to drill-pipes not quite reaching this point when circulating.

Curve 2.—Level lowered just a little below hydrostatic head. The water-sand begins to show up at point *A*.

Note slight diffusion of heat towards bottom.

Curve 3.—Further lowering of level. The water entry is clearly shown and the water fills the hole up to around point *B*.

Diffusion towards bottom again noticeable.

Curve 4.—Further lowering of level. The temperature at point *A* has increased only a little, and is constant up to point *C*.

The temperature effect is noticeable over the entire represented portion of the log.

up by positive temperature anomalies. But let it now be supposed that a well contains a water-sand and a gas (or oil) sand, and that both have actually been produced before killing and circulating the well for the tem-

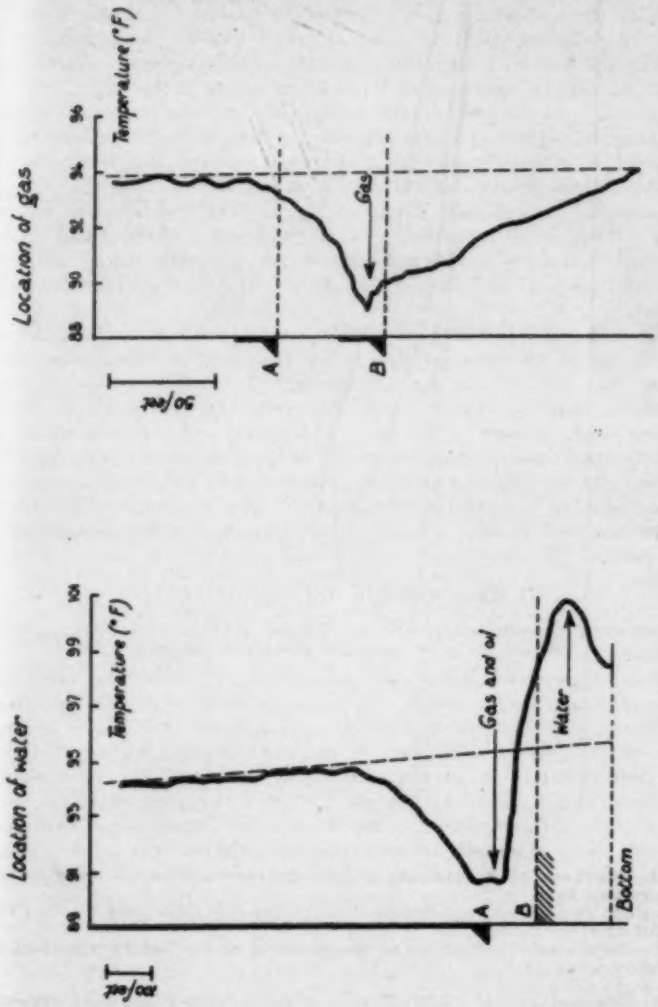



FIG. 5.
LOCATION OF SANDS HAVING PRODUCED WATER OR GAS.

perature run. The water production will not have appreciably altered the natural temperature of the corresponding sand, for the reason just recalled, and this water-sand will therefore continue to cause a positive temperature anomaly. But the gas-sand will now be naturally "cold,"

since gas-expansion, consecutive to gas-production, will have occurred not only in the hole, but also within the layer itself; it will therefore show up accordingly on an appropriate temperature run.

This method is very attractive, not only because there is no necessity to condition the well with a mud of appropriate salinity, but also because there is not even any need to lower the level. Usually just one run will suffice, and the method is therefore rapid, the more so since the circulation can automatically be combined with the actual killing of the well.

The method can be applied either for water-locating purposes, or for determining the portion of a complex which is responsible for an excessive gas production, it being natural that expansion, and cooling, will be most important in those portions which contain most gas.

Two practical examples are shown on Fig. 5. The first concerns water-location. With casing cemented at *A*, the well was completed and made 25 per cent. water. The thermometric survey was then made, and, on its evidence, the well was plugged back to *B*, reducing the water down to 1 per cent.

The second example refers to gas-location. The well was completed with a casing at *A*, and produced during two months. From the very beginning, the gas–oil ratio was already high, but, as time went on, the well became more and more a pure gas well. The temperature curve shows the point of entry of the gas very clearly, and the persistence of the low temperatures for some distance below this point even suggests that some gas may have effectively flowed downwards and penetrated into and "shut-off" the productive oil-sands. A new casing was cemented at *B*, and the well became a good oil producer, with a very satisfactory gas–oil ratio.

## II. Measurements in Cased Hole.

Temperature measurements can also furnish invaluable information in cased holes.

(*a*) *Water Flows and Water Movement behind Casing.* The point of entrance of water into the well at the bottom of or through a faulty string of casing can, of course, be determined by a method identical with that used for open holes (refer to Fig. 4). But a further advantage of the thermometric method is that it determines not only the depth where the water enters the hole, but also that of the sand which is the cause of the trouble.

Fig. 6 shows a theoretical example of such a determination. One sees that if the water is actually entering the hole—for instance at the casing shoe—it really comes from a sand some distance above it. Curve 1 is obtained some little time after circulation and while the level in the hole is still above hydrostatic. According to local features, it may or may not already give a slight indication of the position of the sand. Curve 2 is obtained after having lowered the level somewhat and forced the sand to produce some water, which is seen to be moving down towards the casing shoe. This movement occurs between the casing and the formations, but the temperature effect is transmitted by the casing (steel) to the mud inside the hole. After further bailing, the water behind the casing will reach the shoe, and start moving upwards therefrom inside the hole (curve 3). It will be noticed that, even if there is no actual upward movement of water

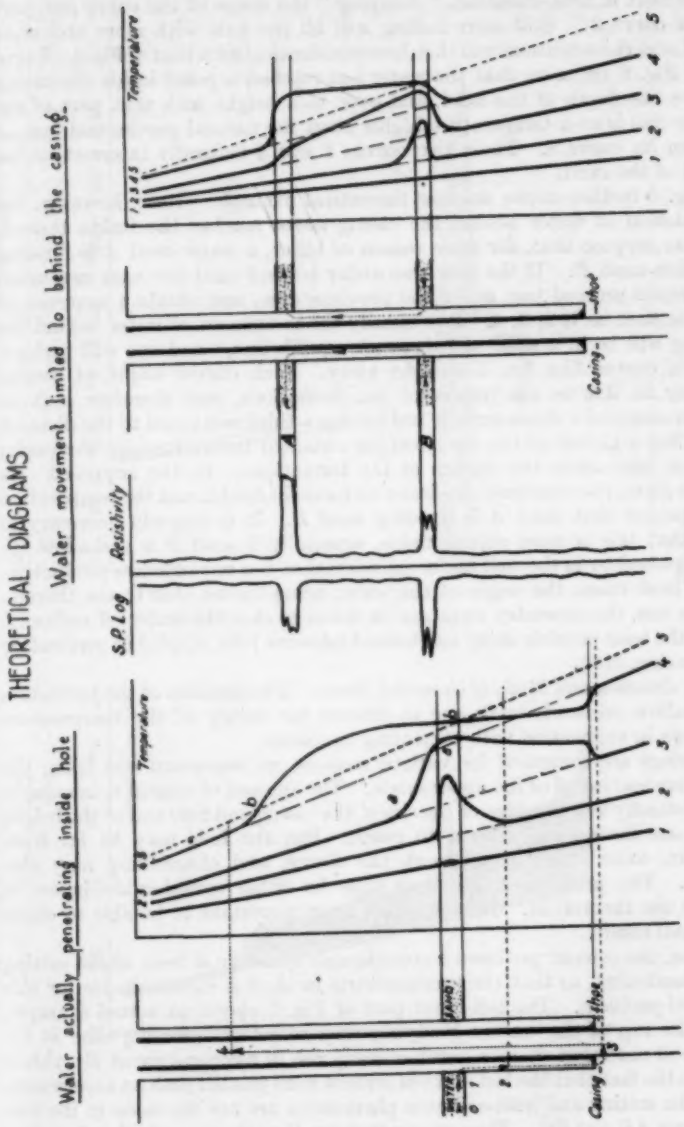



FIG. 6.
LOCATION OF WATER FLOWS BEHIND CASING.

behind the casing and above the sand, the casing itself may serve to transmit some heat in that direction, " damping " the shape of the curve (see part *aa* of curve 3). Still more bailing will fill the hole with more and more fluid, and the conditions will then become identical with that of Fig. 4. Curve 4 of Fig. 6 supposes that the water has reached a point inside the casing above the depth of the sand, and even to a height such that part of the curve (*bb*) is at a temperature higher than the natural geothermal one, as shown on curve 5. These two curves 4 and 5 naturally intersect at the level of the sand.

Fig. 6 further shows another theoretical example. Here, however, the circulation of water behind the casing never reaches the inside thereof. Let us suppose that, for some reason or other, a water-sand *A* is flooding another sand *B*. If the flow was under control (and the case can exist) one could proceed just as for the previous case, and obtain a sequence of curves such as 1, 2, 3, 4. But usually the movement of water behind the casing will be in a state of " dynamic equilibrium," and one will perforce obtain curves like No. 4 straight away. Such curves *might*, of course, merely be due to the nature of the formations, and therefore indicate the presence of a characteristic bed having a thickness equal to the distance *A*. But a glance at the electrical log obtained before running the casing will at once show the nature of the formations. In the supposed case of the plate, the combined logs leave no room for doubt, and the temperature run proves that sand *A* is flooding sand *B*. It is scarcely necessary to add that this is most objectionable, especially if sand *B* is a shallow oil-sand passed by in the well under consideration, but nevertheless productive.

In both cases, the origin of the water being known, due to the thermometer run, the necessary steps can be taken to shut the water off radically, with the least possible delay and hazard (squeeze jobs, ripping or perforating the casing, etc.).

(*b*) *Location and Study of Cemented Zones.* The mention of the protection of shallow oil-sands leads one to discuss the utility of the temperature surveys in connection with cementing problems.

Casings are cemented for various reasons, an important one being the effective sealing off of the upper sands. The amount of cement is calculated theoretically as a function of the size of the casing and hole and of the height that one desires the cement to reach. But the hole may be far from regular, some sands may absorb the slurry, and channelling may also occur. The practical height may thus be either considerably below or above the theoretical. It is therefore most important to be able to check the final result.

Now, the cement produces a considerable quantity of heat whilst setting and hardening, so that the thermometric method is most suitable for this kind of problem. The left-hand part of Fig. 7 shows an actual example, and the top of the cement is clearly seen to be at *A* (casing shoe at *C*). One will note that there is another sharp rise of temperature at *B*; this is due to the fact that the last sacks of cement were treated with an accelerator, and the setting and heat-emission phenomena are not the same in the two portions *AB* and *BC*. The temperature run thus shows up both interesting points. Finally, the rise at *D* is due to the cement existing both inside and outside of the casing just below this depth (plugs not yet drilled out).

Locating top position of caves and study of soundness of cement.

Locating top of cement

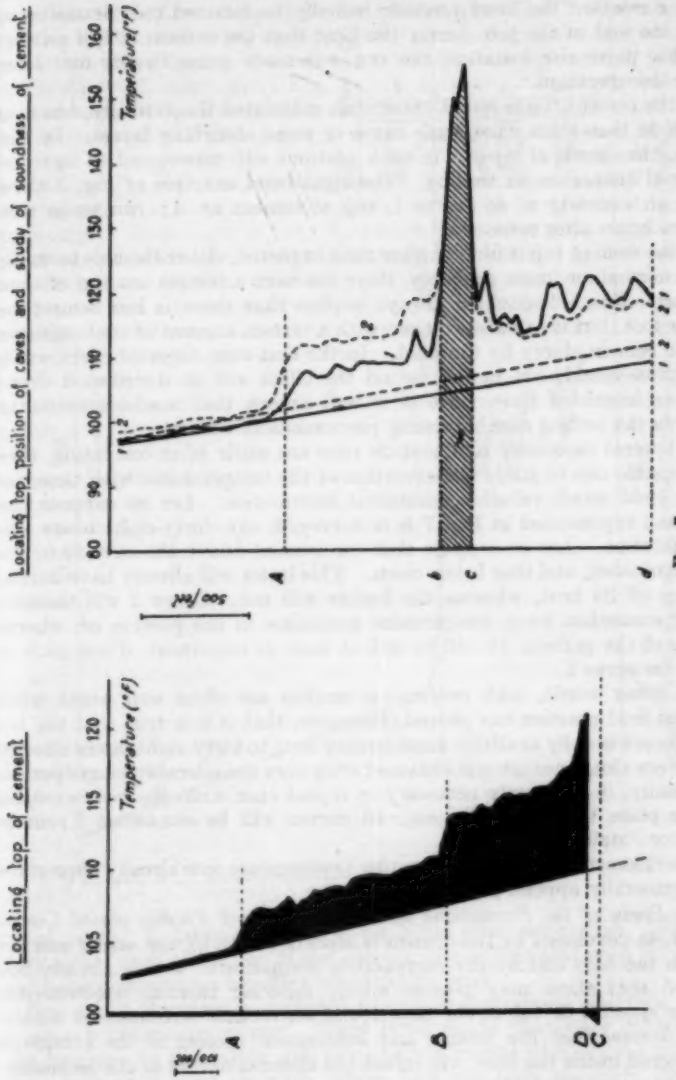



FIG. 7.
CEMENTING PROBLEMS.

The run is best and most easily made whilst standing and waiting for the cement to harden—that is to say, some hours after the operation, and after having released the head pressure (usually maintained only immediately after the end of the job, during the time that the cement is still setting). In this particular instance, the run was made some twenty-four hours after the operation.

If the cement top is found lower than calculated theoretically, one must conclude that there exist some caves or some absorbing layers. In both cases, the excess of cement in such portions will correspond to increased thermal anomalies on the log. The right-hand example of Fig. 7 shows such an anomaly at *bc* (curve 1, top of cement at *A*; run made some twelve hours after cementing).

If the cement top is found higher than expected, either the hole is smaller than normal, or, more probably, there has been a certain amount of channelling. Now, channelling always implies that there is less cement per linear foot, but it can also co-exist with a certain amount of contamination of the cement-slurry by the mud. In the first case, thermal effect will be less pronounced, but in the second the effect will be distributed over a greater length of time, since it is well known that mud-contamination retards the setting and hardening phenomena of cement.

If several successive temperature runs are made after cementing, these will enable one to study the evolution of the temperatures with time, and may yield much valuable additional information. Let us suppose that the well represented in Fig. 7 is re-surveyed, say, forty-eight hours after cementation. Let us suppose that the cement above the cave *bc* is mud contaminated, and that below clean. This latter will already have finished giving off its heat, whereas the former will not. Curve 2 will therefore show somewhat lower temperature anomalies in the portion *cd*, whereas those of the portion *Ab* will be still at least as important, if not more so, than on curve 1.

In other words, such evolutional studies are often well worth while. Actual field practice has proved, moreover, that if it is true that the best results are usually available some twenty-four to forty-eight hours after the job, very clear ones are still obtained after very considerably longer periods.

Finally, it is scarcely necessary to repeat that since the heat exchange takes place through the casing, all curves will be somewhat " rounded off " or " damped " thereby.

Thermometric studies of cementing problems are now already appreciated and generally applied in several countries.

(*c*) *Study of the Formations through Casing and Freshly-placed Cement.* The heat developed by the cement is absorbed both by the casing and mud inside the hole and by the surrounding formations. It has already been stated that these may possess widely differing thermic conductivities, either specific, or due to the presence of convection currents. It is therefore natural that the setting and subsequent cooling of the cement, as registered inside the hole, will reflect the thermal nature of the formations. Highly convective water sands may, for instance, perhaps retard the setting and heat emission phenomena of the cement, and will also allow the calories generated by the cement to escape much more easily than the less conductive shales.

The temperature run will thus show anomalies which will be related to the stratigraphical sequence of formations. A very vivid example is

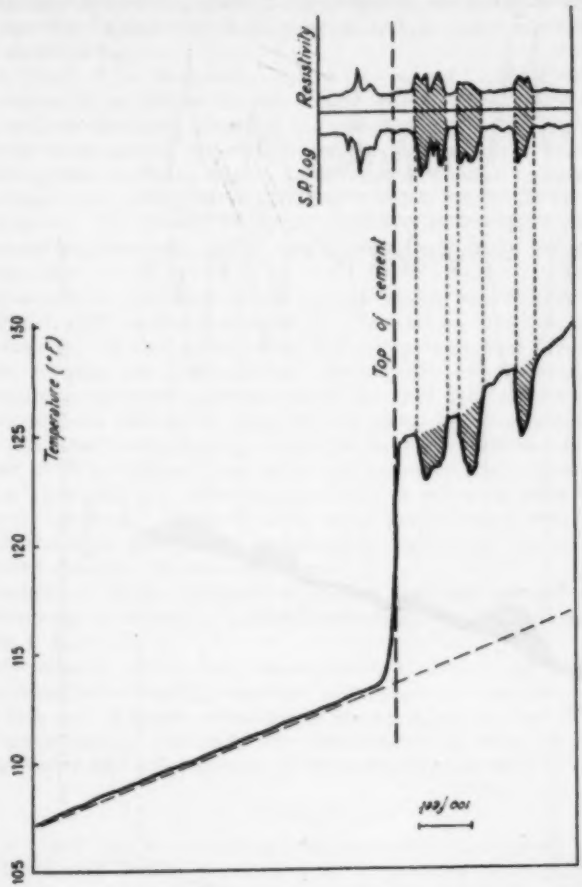



FIG. 8.
STUDY OF FORMATIONS THROUGH CASING AND FRESHLY-PLACED CEMENT.

given on Fig. 8, taken some thirty-six hours after cementing. Besides a very clear check of the top of the cement, one notices that each important sand corresponds to a negative temperature peak.

One might therefore be tempted to replace the normal electrical log by a mere temperature survey. There is no doubt that some information can be given by this latter, and cases have occurred when such a run gave very important data on wells which had not been regularly surveyed before running casing. But it has already been explained why a temperature run is generally less detailed and accurate than an electrical log (damping effect; possible proximity to point *X* of Fig. 2, where temperature

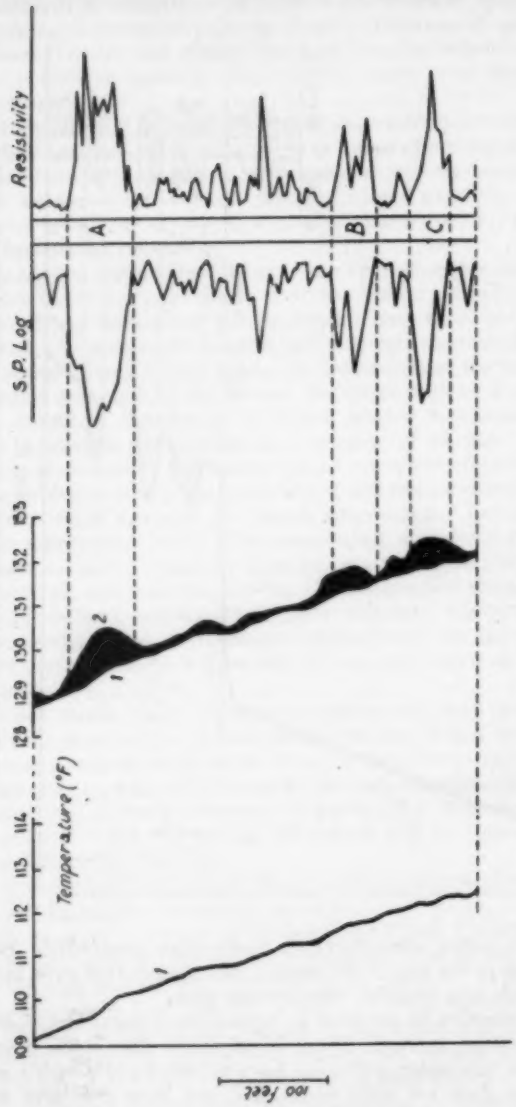



Fig. 9.

STUDY OF FORMATIONS THROUGH CASING AND "OLD" CEMENT.

anomalies are necessarily small, etc.). Likewise, temperature anomalies, in such cases, may be due either to formation influence or to irregularities in the cement itself (see above). Their proper and accurate interpretation can therefore be made only if one possesses and can compare the temperatures and electrical logs.

(*d*) *Study of the Formations through Casing and "Old" Cement.* When the cement is no longer the seat of any thermic effect of its own, results may still be obtained, although the presence of both casing and cement calls for more careful operating technique, on account of their combined screening and damping action. But experience has repeatedly proved that this action of the casing, with or without cement, is far from being prohibitive. The general principles explained above, and especially those discussed together with Fig. 2, can therefore still apply and give reliable information.

An example of measurements through casing has already been given on Fig. 1. Fig. 9 shows another very interesting example, inasmuch as an electrical log was made before cementing the casing, over two years before running the thermometer. Preliminary circulation lasted some six hours in this particular case, since the mud had to have time to cool the formations themselves, through the casing and the cement. Special care was taken in keeping the circulation as regular and as cold as possible (about 60° F.). Curve 1 was taken almost immediately after circulation, and is therefore, and quite rightly, flat. A series of other curves was taken at intervals. Curve 2, taken some twelve hours after circulation, shows the most pronounced temperature variations. Curve 1 has been re-drawn alongside for easier reference.

Comparison of the blackened-in portion between curves 2 and 1 with the electrical log shows a remarkable correlation opposite the major porous layers *A*, *B* and *C*.

This example shows that thermometric technique can yield data on formations behind casing, cemented any length of time previously. The best data are, of course, available on the electrical log, but if such a run was unfortunately not made, for some reason or other, a temperature run will often allow the operator to cut down his guess-work to a minimum.

## Conclusions.

It is hoped that the preceding major examples have served to show the extremely wide field of application of temperature measurements in oil-wells, both in open hole and through casing.

In practice, one has to contend with several what may be termed "disturbing influences," only some of which may be eliminated at will. Amongst these latter, one can mention the time, speed and temperature of preliminary circulation, and the carrying down of the circulation to the very bottom of the portion to be surveyed. But other factors exist, over which one has but little or no influence: bottom-hole effect in drilling wells, size of the hole, nature of the fluid in the hole (a viscous mud will, for instance, give rise to less convection within itself), etc.

For all these reasons, and also because of the numerous natural causes of thermal anomalies, the technique of operation and the interpretation of temperature diagrams must be considered as an art.

The best results are obtained with unreserved co-operation between the surveyor, who possesses a wide and general experience of temperature measurements, and the field staff, fully aware of the particular conditions of each local problem. Together, these two can elaborate beforehand the best technique to be applied, and afterwards discuss the results.

The field staff must understand that quite a number, though certainly not all, temperature surveys may require some time. One may hesitate as to whether one should apply the method or not, but once the decision has been taken, over-much haste to have the well "free" once more may lead to obtaining no useful result whatever.

Finally, it will be noticed that the best results in wells not in thermal equilibrium are obtained at different lapses of time after circulation, according to local conditions. Experience has happily proved, however, that this optimum time is very soon determined for a given region and for a certain normal type of problem.

In conclusion, the authors wish to acknowledge the kind collaboration of numerous oil companies during the experimental stages of this now-proved technique, as well as permission to reproduce some actual diagrams. It will be noticed that all relevant data on the wells and fields have been purposely omitted.

## *DISCUSSION.*

PROFESSOR V. C. ILLING said that the name of Schlumberger had become almost a household word in the oil industry, owing to the help which they were giving nowadays to those engaged in that industry. The name was associated more particularly, of course, with the use of the resistance log in correlation work, a method which had proved an immense boon to geologists in many oilfields. The authors had indicated that they were turning their attention to other directions in which applied physics could help the industry.

Many points rose to his mind in connection with the new development described in the paper. First of all, there was the ingenuity of using the electrical resistance thermometer as the method of temperature measurement. Those who were interested in earth temperatures were conversant with the unsatisfactory data at present available for scientific study. It was an extremely difficult matter to get really accurate temperature measurements within the crust, and he felt that the authors were to be congratulated on their choice of the resistance thermometer as the ideal instrument and the manner in which they had overcome difficulties in rendering it available for service.

An interesting point was the question of the reduction in the temperature gradient near gas sands. He presumed that, in making these comparisons, the authors assumed a normal average temperature gradient downwards and related their results to this presumed gradient. Would it not, however, be a fact that the average gradient was itself a function of the conductivity, and therefore opposite gas sands, the conduction of which would be low, the gradient would be lower than the normal in any case?

MR. A. BEEBY THOMPSON said the methods described in the paper were somewhat new, but of great value to those engaged in the oil industry. When engaged on oilfield work in the past, he had frequently noted differences of fluid temperature in wells, and had never been able to interpret them to his satisfaction. He had naturally considered that the gas escaping from the liquid was partly, if not mainly, responsible for the temperature variations. One would have surmised that heat diffusion would have masked earth temperatures within the limits of observation, but it was clear that if the authors' instrument would record such small differences, it would be of enormous assistance to those engaged in the oil industry. As the Chairman had said, one of their greatest difficulties in the past had been to correlate beds in the Tertiary strata; indeed, it had never been done satisfactorily until the introduction of Mr. Schlumberger's methods. He thought Mr. Schlumberger's work in electrical coring and also in temperature recording was likely to revolutionize oilfield practice; it would certainly remove many of the uncertainties and troubles that had been experienced in the past by oilfield operators.

PROFESSOR O. T. JONES said he was very interested in a method of registering accurately the temperature at various depths in the crust. There were two points involved. The one which the authors had been mainly considering was the case of temperature which was in a state of flux; in other words, it had not steadied down. The other point was also of great interest to geologists and those considering the history of the earth in the past—namely, the rate at which the earth was losing heat. There seemed to be the most extraordinary diversity of views on that question. It used to be thought that the difficulty was that one did not know enough about the conductivity of the rocks in the crust, and that therefore, owing to the uncertainty of that factor, one could not really say for any given hole at what rate heat was escaping from the crust itself. That heat which was escaping probably in part belonged to the earth itself of old time, and was probably manufactured by the radioactive substances in the outer crust of the earth, and, until the rate at which heat was escaping in a large number of places, not merely one or two, was known, one could not really tell whether the heat that was now escaping from the earth was more or less than the heat which was being generated all the time in the crust. In other words, one did not know whether the earth was becoming hotter or cooler. As he had said, it used to be thought that the difficulty in estimating the heat lost was due to a lack of knowledge of the conductivity of the rocks in the crust, but that was not the difficulty. The great difficulty now was to get accurate temperature measurements. If those measurements could be obtained, far better estimates could be made of the rate at which the earth was losing heat.

Turning to the question of wells in which the fluid was not in thermal equilibrium with its surroundings and in which heat was escaping from the materials in the sides at a considerable rate, the indications given in the paper of differences in the nature of materials were extremely interesting, but it occurred to him to ask what was the reason for those differences. It might be the thermal conductivity itself of, say, wet

sands in comparison with other materials; but might not the reason also be found in the fact that circulation of water was taking place in those sands, and therefore the heat was being carried out from the sands into the mud or into the sides of the well? The water would carry heat with it by direct convection. But he would like to know whether, in the case of a gas where there was a temperature drop, it was really a temperature drop due to the expansion of the gas, or was it merely due to the fact that nothing was coming out to carry the heat, because gas itself would not carry very much, and there was no circulation in the material around the hole?

Captain D. Comins thought that the method described of locating the height which cement had risen behind the casing after a cementing job would be new to most members, and should be of considerable practicable application.

The estimation of the actual position of oil, gas and water shown in wells by thermometric methods was a subject on which his Company in Iran had had no actual experience, although they had done a good deal of temperature work. He could, however, scarcely believe that the temperature opposite an oil horizon would always necessarily be low, as was claimed in the paper. It would be low only after gas came out of the solution from the oil at that point, and gas would not come out if the back pressure on the drilling fluid of the formation was greater than the saturation pressure of the reservoir crude.

The experience of his Company in Iran had been on rather different lines. They had started by taking temperature measurements with the idea of trying to correlate temperature gradients and isogeotherms with structure, and they had obtained some very interesting results. They found that over a greater part of one field the gradients were always low on the top of the structure and high on the flanks, the gradients varying from 4° F/1000 feet to 8° F/1000 feet. They therefore thought that they could forecast structures to some extent, but they found that in other areas exactly the reverse applied, and higher gradients were observed ranging up to about 15°/1000 feet. They had therefore abandoned the geothermal method of estimating structure, as it was uncertain to which geothermal category a new area would belong until a number of wells had been drilled, by which time the information was not of much practical value.

They used temperature measurements a great deal, however, as subsidiary to other physical observations. Such measurements were essential in using the bottom-hole pressure indicator, of the type in which the method of compression of air was used. They were also essential in bottom-hole sample taking, as it was necessary to know exactly the temperature in the reservoir, so that the saturation pressure of the reservoir crude could be measured at that temperature. Also the measurement of the physical properties, specific gravity, viscosity, surface tension, and so forth, had to be carried out at the actual reservoir temperature.

The continuous survey of temperatures as well as pressures in flowing wells from top to bottom was essential for energy calculations. His Company did not, however, use recording thermometers for this purpose.

They had one, but it was too large for use in flowing wells, and, instead, they took readings at intervals with maximum thermometers.

The recording thermometer described by the authors of the paper would, however, be very suitable for this purpose, being of small diameter, provided the insulated cable was suitable for running in against high pressures, and did not deteriorate rapidly after use in oil.

It would be clear from the applications he had mentioned that his Company found temperature measurements of value, and he therefore welcomed the advances in technique reported in the present paper.

He had been very much surprised to see in one of the diagrams that had been shown the very sharp change of gradient found in passing from one formation to another. He himself had never observed such a sharp change, and asked whether the occurrence of such a change had been confirmed by observations in other wells.

His Company had no experience of the thermal evolution method described in the paper, which seemed very interesting indeed. They had always waited for thermal equilibrium to be reached. One fact that his Company had found was that in an ordinary rotary well the only reliable reading of the earth temperature was at the bottom of the well after it had been shut down for one week. They had also found that there was very little convection in oil wells.

He would like to know what pressure the insulated cable of the author's instrument could be run against. That was rather an important point as regards the practical application of this resistivity method of temperature measurement, which he agreed was far more sensitive than the measurement by ordinary maximum thermometers, or by Bourdon Tube Type Recording thermometers.

Mr. Charles Dabell said he believed it was on record that in a Mexican field where careful temperature recording was carried out the advent of water was anticipated by the increase of temperature in the oil produced. He had had personal experience of this in the Argentine, where it had been possible to anticipate the advance of water by a gradual, slow but sure increase in the temperature of the oil being produced.

Mr. B. J. Ellis said he was sure no one doubted the statements made in the paper, but it might interest the members if he gave them some corroborative evidence. His Company had had a number of temperature surveys taken in Burma by the authors' apparatus, particularly with the object of determining the height to which cement had risen, and in each case that information had been obtained. His Company had been having a number of cement failures which were rather difficult to understand, and, by means of the authors' temperature recorder, it had been discovered that the cement was rising behind the pipe to a much greater extent than it should have done. That indicated channelling, and his Company found that, by increasing the rate of circulation of the cement and taking steps to whirl the cement, they could prevent the channelling. The height to which the cement rose after those steps had been taken was indicated by the Schlumberger temperature survey to be slightly less than the calculated height.

PROFESSOR A. O. RANKINE said that to a physicist the obvious method of measuring temperature in an inaccessible spot, such as a deep well, was by the use of the platinum resistance thermometer, and when Captain Comins was making his measurements about nine or ten years ago, the question arose as to whether such a thermometer could not be conveniently employed; but for the deep wells with which the Anglo-Iranian Company were concerned it was concluded that the device would be too cumbersome. The authors gave in their paper very little detail regarding their apparatus; it was not even mentioned whether they had followed Callendar's procedure, employing a platinum resistance coil and the usual compensating leads. Could they say what was the weight of their cable per unit length? Did it carry four leads, two of which were compensating leads, as in the normal Callendar method of eliminating the effect of temperature on the leads themselves, as distinct from the platinum? If so, it seemed as though it would need to be fairly weighty and of considerable strength to support its own weight, especially in very deep holes.

MR. E. S. L. BEALE thought that the cable used in the authors' instrument must be a very highly developed type. It had to do a great many things. It had, he supposed, to carry four leads, it had to be strong, and it had to have a good insulation resistance and to be capable of maintaining that insulation resistance in contact with salt water and oil, so that a number of normal types of insulating material were ruled out. He imagined that it also had to present a smooth external surface, so as to be run in through a gland against pressure, and maintain the gland gas-tight. It would be very interesting indeed to have a few particulars of the cable.

PROFESSOR V. C. ILLING said that it was clear from the discussion on the paper that it had a wide appeal. The physicist was interested in the details of the instrument and how the difficulties had been overcome. The geologist was interested in it as a means of throwing light on the temperature gradients within the crust and the engineer had found in it a valuable ally in many of his field problems.

THE AUTHORS, in replying to the discussion, stated that the cable was the same as that used for electrical logging, and comprised three stranded and insulated steel conductors. Such a cable was perfectly satisfactory, except in cases where the well was filled with excessive quantities of gas or oil, which were detrimental to it. The tensile strength varied from 2 to 8 tons with the type of cable, the corresponding weight varying from 300 to 700 kgs. per kilometre.

CAPTAIN COMINS inquired further as to whether the cable was armoured and whether it could be run through a gland against pressure. The AUTHORS replied that the cable was only braided, inasmuch as armouring would make it very difficult to locate electrical leaks. A special stuffing-box had been devised for use with the cable and, unless very unfavourable

working conditions were present, the authors believed it quite possible to run against pressures of up to about 1000 lbs.

Replying to Captain Comins' remark on the abrupt change of gradient shown on one of the diagrams, the AUTHORS stated that the ratio between the two gradients agreed quite well with the conductivities of the two formations, as given in various scientific tables. A great number of such examples were not available as yet, since they required the existence of sufficiently thick and homogeneous layers, which were not always present in oilfield formations.

With regard to various speakers' remarks on the apparent negative temperature anomalies found opposite oil and especially gas-sands, the authors stated that they quite agreed that such anomalies were not always bound to occur in every single possible case. But the fact remained that they and their colleagues had effectively noticed them in a great number of cases, opposite those portions of the well which had later given gas or oil. The practical value of such anomalies was therefore, in their opinion, already great, and they hoped that, as time went on and more data were collected, it would be possible to study this question more fully from every point of view, they themselves being moreover already convinced of the importance of convective movements in porous layers in all these phenomena.

The following papers were then presented by Dr. J. H. Jones:

"A Method of Testing Reflection Seismographs." By J. H. JONES, Ph.D., D.Sc.

"The Use of Reversed Refraction Arcs in Seismic Surveying." By R. DAVIES, M.Sc.

# A METHOD OF TESTING REFLECTION SEISMOGRAPHS.

By J. H. Jones, Ph.D., D.Sc.

During the course of some experimental work on the application of the seismic reflection method in Iran, the writer proposed a scheme for testing the efficacy of a mechanical seismograph for recording reflected wave pulses.

Difficulties had been experienced by some members of the Staff in the interpretation of reflection seismograms recorded with the mechanical instrument, and it was considered desirable to devise a method of simulating the actual reflection experiment under conditions which could be easily controlled. It should be mentioned at the outset that the reflection method then in use in Iran differed somewhat from that developed and practised in America. The principal difference was in the range at which the reflections were recorded. The early reflection work by the Geophysical Staff of the A.-I.O. Co. was based on the assumption that the reflected wave pulses would show maximum amplitudes near the critical angle. It appears, however, that in practice somewhat greater amplitudes are obtained nearer the explosion point. But there is another reason why it is usually easier to record reflections at small angles than at the critical angle. The critical angle reflection pulses from medium depths strike the surface at distances ranging from 5000 ft. to 10,000 ft. from the explosion point. At these distances several well-developed refracted wave pulses from upper beds may be arriving at the surface at about the same time, so that the motion recorded with the seismograph will be a mixture of reflected and refracted wave pulses.

This compound motion must be analysed and the reflected wave pulse must be identified by virtue of (1) its greater amplitude, and (2) its greater apparent velocity along the horizontal surface. The apparent velocity along the horizontal surface of the critically reflected wave pulse will be identical with the true formational velocity if the reflecting formation is horizontal. It is evident, therefore, that the application of the two criteria mentioned above will only reveal the pulses reflected from formations which possess high wave velocities.* The advantages claimed for the method of recording near the explosion point are two-fold. In the first place, there will be no well-defined refraction pulses to cause interference with the reflections, and secondly, the apparent velocity of the reflected pulses along the horizontal surface will be very much higher.

On the other hand, at short distances from the explosion there is often considerable interference due to the so-called "ground roll," which is a type of very low velocity surface wave. Thus, in the one case there is interference

* In some cases where confusion occurs due to the multiplicity of reflections this would be a distinct advantage.

caused by refracted waves travelling with velocities slightly lower than the apparent velocity of the reflected wave, and in the other, interference due to the low-velocity surface waves. The experiment which we shall now describe is a simple means of investigating the resolving power of reflection seismographs operating under the conditions of interference discussed above.

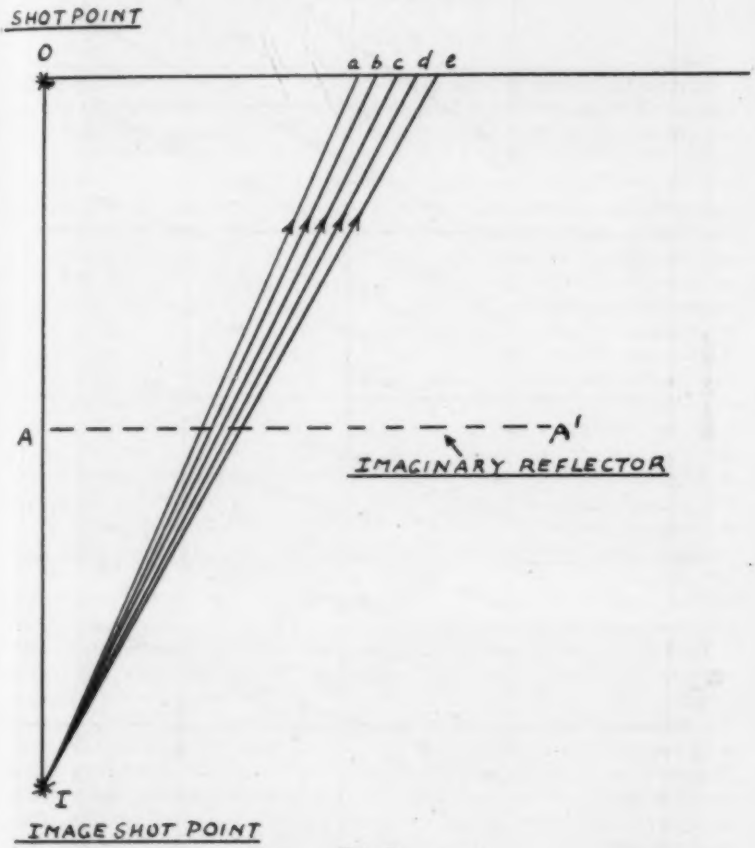



FIG. 1.

METHOD OF TESTING SEISMOGRAPHS.

In the particular test conducted in Iran, the Jones seismographs were laid out in the usual manner in reflection work at intervals of 150 ft. apart; the nearest instrument being about 7500 ft. from S.P.O. (Fig. 1). A charge of 55 lbs. of gelignite was fired at *O* and seismograms were recorded at *a*, *b*, *c*, *d*, etc. Examples of these records are shown in Fig 2*a*, and the time-distance graphs constructed from these seismograms are given in

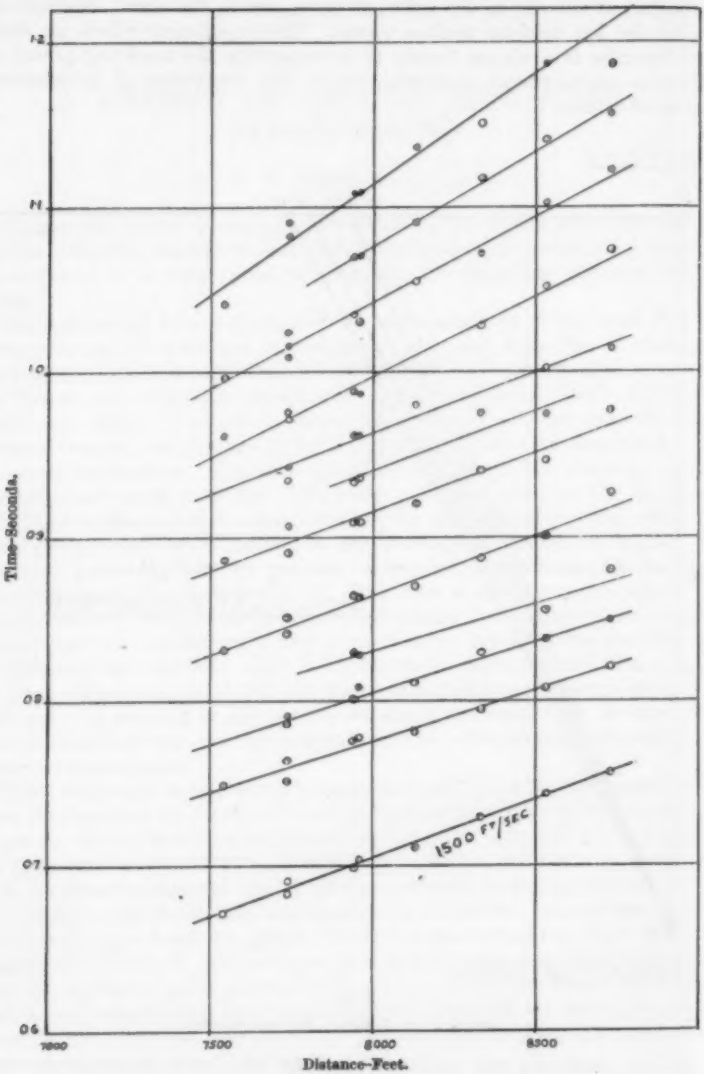



FIG. 3a.

S.P.O. CHARGE, 55 LBS.

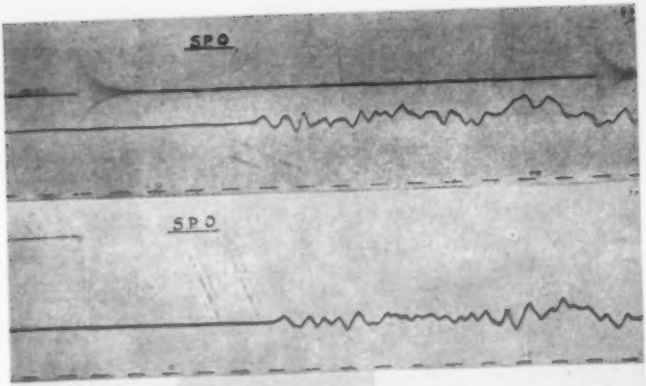



FIG. 2A.

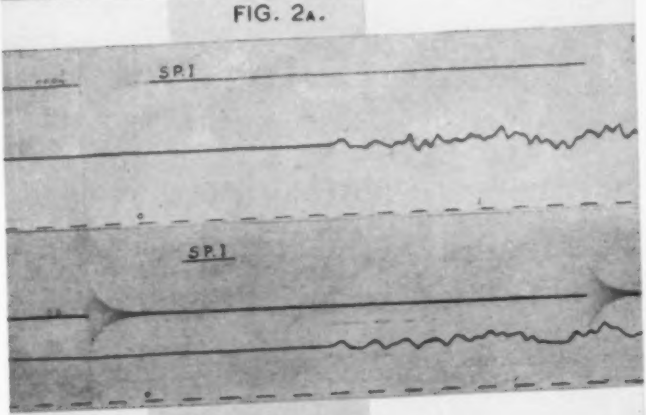



FIG. 2B.

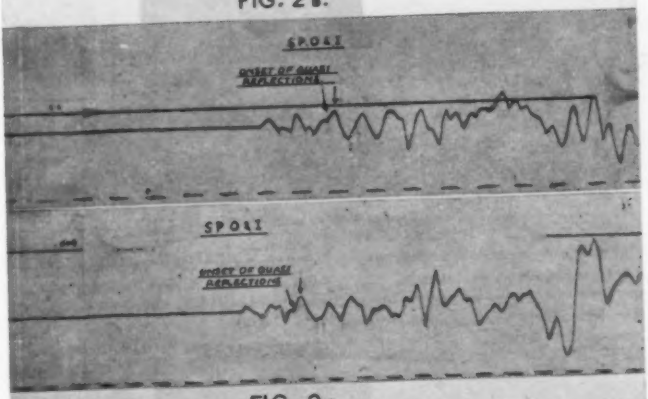



FIG. 2c.

[To face p. 28

UNIV. OF MICH.

Fig. 3*a*. The velocities shown in the graphs are normal formational velocities, possibly slightly affected by small dips of the formations.

The next operation was to fire a similar charge (55 lbs.) at the point *I*, which was located at 9000 ft. on the perpendicular line *OI*. For reasons which will appear clear later, this point is called the " Image " Shot Point. It was found that the charge of 55 lbs. at *I* produced very poor seismograms at *a*, *b*, *c*, *d*, etc., and it was necessary to increase the charge to 100 lbs. to get readable seismograms. Examples of these seismograms are shown in Fig. 2*b*, and the time–distance graphs are plotted in Fig. 3*b*. On these

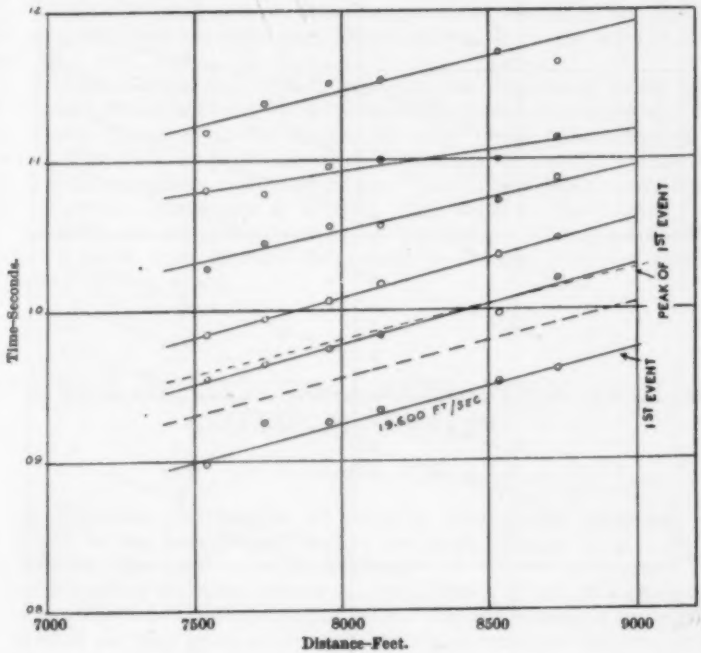



FIG. 3*b*.

S.P.I. CHARGE, 100 LBS.

graphs, the distances plotted are the same as those in Fig. 3*a*, namely, *Oa*, *Ob*, *Oc*, etc., but the times are those taken by the various pulses along the paths *Ia*, *Ib*, *Ic*, etc. Thus the velocities shown on the 3*b* graphs are the phase velocities along the line *Oabcde* of the waves originating at *I*. We may regard the wave pulses arriving at *a*, *b*, *c*, etc., as being reflected from an imaginary layer perpendicular to, and bisecting the line *OI*.

The point *I* is the " image " of *O* in this imaginary reflector. The depth of this imaginary reflector is 4500 ft., and the phase velocities of the quasi-reflections is about 19,600 ft./sec. The next step was to fire the charges at *O* and *I* simultaneously, so that the disturbances reaching the seismo-

graphs at *a*, *b*, *c*, *d*, etc., consisted of the normal movements due to the refracted waves set up by the explosion at *O*, and of the quasi-reflections from the imaginary surface *AA'* set up by the explosion at *I*.

The problems presented in the compound seismograms are: (1) is it possible to detect the quasi-reflections without unduly increasing the image

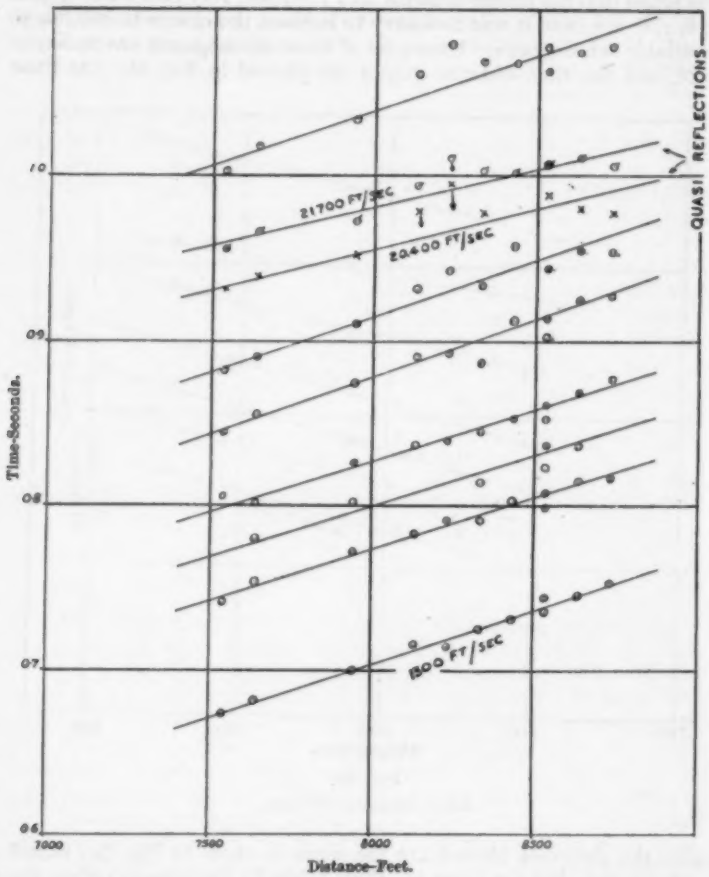



FIG. 3c.

S.P. O. & I. CHARGE, 55 LBS. AT O; 150 AND 250 LBS. AT I.

charge; and (2) with what accuracy can the depth *OA* of the imaginary reflector be determined? In the simultaneous exploding of the charges three different charges were used at *I*. These were 100 lbs., 150 lbs. and 250 lbs. The charge at *O* was kept at 55 lbs. throughout. Examples of the compound seismograms are shown in Fig. 2*c*, and the corresponding time–distance graphs are plotted in Fig. 3*c*.

An analysis of the compound seismograms shows one high-speed event which we believe corresponds with the initial onset of the quasi-reflections. Reference to Fig. 2*b* shows that the beginning of the quasi-reflection movement is rather ill-defined. For this reason we have also measured, as a further check, the time to the first peak, which happens to be much better defined.

These are the first two sets of points shown on Fig. 3*b*, and both show a velocity of about 19,600 ft./sec. On the compound seismograms 2*c* we have marked the nearest approach to the poorly defined beginning and the first peak of the quasi-reflections.

The time–distance graphs of these two events are shown in Fig. 3*c*, and the same two lines have also been plotted on Fig. 3*b* for purposes of comparison.

It will be observed that there is an appreciable discrepancy in the time of the onset of the quasi-reflection, but excellent agreement in the time of the first peak. The error in the time of the onset of the quasi-reflection is about 0·03 second, which is equivalent to an error of about 220 ft. in the depth of the imaginary reflecting surface. The actual depth deduced from the compound seismogram is 4720 ft. The error in the "depth" is undoubtedly caused mainly by the poor beginning of the quasi-reflection event. A much more accurate value could be deduced from the time of arrival of the first peak.

# THE USE OF REVERSED REFRACTION ARCS IN SEISMIC SURVEYING.

By R. Davies, M.Sc.

The Refraction Arc method of mapping underground structure, as developed by the Geophysical Staff of the Anglo-Iranian Oil Co., Ltd., has been fully described by Dr. J. H. Jones.*

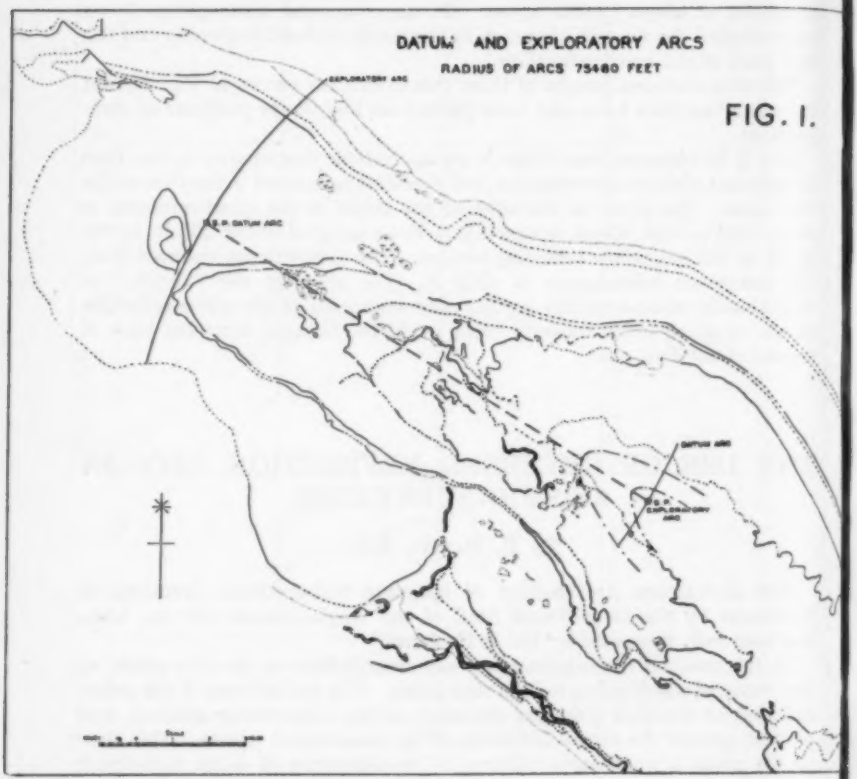
In this method the seismometers are arranged on an arc of a circle, at the centre of which is located the shot point. The travel times of the pulses initiated at the shot point are recorded at the seismometer stations, and plotted against the arcual distances of the observation points. This time profile gives a qualitative picture of the structure of some underlying medium.

This medium can be identified provided, firstly, that the true velocity of the pulse plotted on the time profile can be determined, and secondly, that this velocity can be correlated with that determined on outcrops, or over some well-defined vertical section. Thus, in most refraction arc surveys it is essential to have at least one linear refraction traverse of a certain critical length surveyed in both directions. From the time curves of this traverse the true velocity of the plotted pulse can be determined, and the time profile can be identified with some underlying medium. This,

* A Seismic Method of Mapping Anticlinal structures. Proc. World Petr. Congr., 1933, I, 169.

in turn, can usually be correlated with some known geological bed or group of beds.

In the following note is described the adaptation of this method of seismic surveying to the exploration of an area which presented certain difficulties to the ordinary application of the method. In this area the uncertainty of the strike of the underlying structure rendered the shooting of linear




traverses for the purpose of obtaining the necessary velocity data highly speculative.

The problem was, however, simplified by the fact that, at about 15 miles distance from the area to be explored, the underground structure had been well defined by drilling. The method by which the information on the known section was utilized in the seismic exploration of the new area by means of reversed refraction arcs is illustrated in Fig. 1, which shows the layout of the " datum " and exploratory arcs.

The shot point of the datum arc was located in the area to be explored, and the arc described over the known section. This involved observing at

FIG. 2.

EXPLORATORY ARC

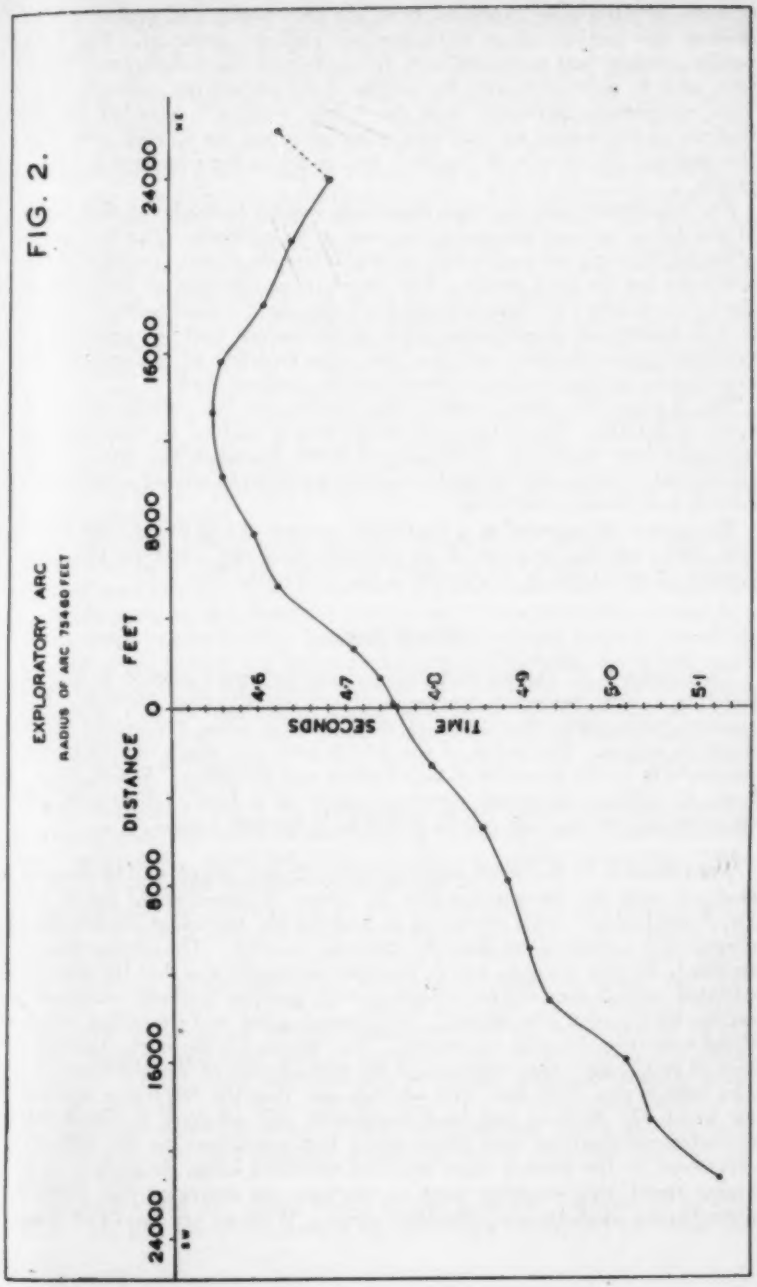

EXPLORATORY ARC
RADIUS OF ARC 73480 FEET
DISTANCE FEET
0
8000
16000
24000
8000
16000
24000
TIME SECONDS
4·6
4·7
4·8
4·9
5·0
5·1

FIG. 2.

stations situated over 75,000 ft. from the shot point, and probably constitutes the longest radius refraction arc hitherto surveyed. The time profile obtained was compared with the section of the underground structure, and, in particular, with the profile of the underlying reservoir rock. This comparison indicated that the "first arrivals" recorded at the stations on the datum arc had been refracted along the oil rock, and that the position of the axis of this rock bed could be deduced from the time profile.

The exploratory arc was then described, passing through the shot point of the datum arc and traversing the area to be explored. The shot point of the exploratory arc was located on the datum arc close to position of the minimum on the time profile. The travel times recorded at the poles of the two arcs were 4·755 seconds and 4·757 seconds. This agreement, which is well within the experimental error, demonstrates that the principle of reversible paths obtains, and that the pulse recorded at the pole of the exploratory arc had been refracted along the reservoir rock.

Fig. 2 shows the time profile of the exploratory arc, which covered a span of 9 miles. From the most south-westly station to the point of minimum time there was a decrease of 0·570 second in the travel time. North-east of the minimum there is an increase of 0·134 second in the travel time in a distance of 10,000 ft.

The profile, interpreted as a qualitative picture of the underlying structure, indicates the presence of an anticline with one point on the axis, located about 13,000 ft. north-east of the pole of the arc.

## *DISCUSSION.*

PROFESSOR V. C. ILLING said that Mr. Davies' paper seemed to him to describe a very ingenious extension of the arc shooting method. The speaker could argue that it would work in some cases, but would break down in others. The paths of the waves were not absolutely identical, particularly at the extremes of propagation and reception. Where, therefore, an oblique geological structure, such as a fault, intersected the structure at one end, the results would be in no way similar.

PROFESSOR A. O. RANKINE, referring to Mr. Davies' paper, said he thought that not only Mr. Davies, but also Dr. Jones, deserved credit for it, for Dr. Jones had also been concerned in devising the particular method here described of searching out into the unknown country. The results seemed to him to be very striking, and he thought the reason was that the method adopted—which was old as compared with modern methods—depended on the timing of a *first* arrival. No question arose as to selecting something appearing later in the record. The points on the curve therefore had no ambiguity; they represented the first arrivals at the seismometers. The reason why they were first arrivals was that the refraction method for which Dr. Mintrop had been responsible was adopted, in which the disturbances observed were those which had gone down to the bedrock (limestone in the present case) and had travelled along its surface at a higher speed, thus enabling them to overtake the slower-moving surface disturbances at distances sufficiently great. With an arc radius of nine

or ten miles, such as Mr. Davies had used, that condition of affairs would operate; it would not do so at too short a radius.

As he had said, he thought the reason why the results were convincing was that there was no demand that one should pick out, from among the intricacies of a seismographic record, some particular new event. It was on that account that he felt rather critical about Dr. Jones' paper. He thought Dr. Jones' idea of testing the question of the possibility of observing reflections was a really clever one. The difficulty about observing reflections was that they were bound to arrive after the initial disturbance, and, if the seismograph had already been thus agitated to a large extent, unless one was able sufficiently to suppress this agitation, it would be almost impossible to detect the relatively feeble effects of reflections. He knew that in the reflection method as normally practised with electrical seismographs something could be done in the direction of preferential treatment as between the direct or surface wave and the reflected wave, but in the case of Dr. Jones' own mechanical seismograph (which in his view was one of the best that had ever been constructed, and fulfilled the conditions of a good seismograph better than most) there was no provision for giving that preferential treatment, and therefore, without that aid, Dr. Jones had still to select the reflections from the complicated records.

It seemed to him remarkable that, although the amount of explosive which had to be used at the quasi-image point was so large in relation to that used at the original point that it gave a disturbance of amplitude virtually equal to that from the first source, it was not more obvious as a new arrival. Quite frankly, he could not have selected those points which Dr. Jones had picked out, although he admitted that Dr. Jones had much more experience in the matter than he had himself. He felt convinced, therefore, that in the case of actual reflections, the intensities of which were generally much smaller than those of the direct disturbances, the difficulties of discrimination would be too great for an investigator even so highly skilled as Dr. Jones.

The diagrams in which the results were plotted were also unconvincing, for the distribution of the crosses relating to the supposed quasi-reflections was, in his view, much too distorted for any justifiable attempt to be made to draw a straight line through them.

He thought Dr. Jones ought to say frankly that the experiment was a failure. It was a well-conceived experiment, and one which might very well be adopted as a test method by those who used electrical seismometers and recording, on account of the preferential treatment which was there possible, as already mentioned. He thought Dr. Jones' method might provide a sound means of discovering whether the multitude of events which hitherto had been called reflections were really genuine. He was sure that, if the subject was to be put on a really satisfactory basis, those engaged in it must be more critical than some of them were inclined to be, and that they should reject those observations which did not fulfil the mathematical and physical conditions which were the basis of the method itself.

He hoped that Dr. Jones would forgive him for speaking as he had done. He had every admiration for Dr. Jones' work, but he could not

accept his interpretation of the results obtained by his elegantly devised method now described.

MR. LANCASTER JONES said that the two very interesting papers which had been presented by Dr. Jones undoubtedly had an importance which was perhaps not apparent. The authors dealt with technique, and were concerned solely with the technique, but the importance of the papers, to his mind, lay in the ability of the particular instrument invented by Dr. Jones to do a certain type of work.

With regard to Mr. Davies' paper, he was not quite clear how one got from the exploratory arc to the datum arc. He presumed that the method of arc shooting implied that if one shot along an arc, one got the time profile, and he would have thought that if one shot along the exploratory arc, one would get the profile; but it was probable that there was some underlying assumption of homogeneity of the surface involved in arc shooting, and that the reversed arc test was a method of testing that the surface was homogeneous. He took it that actually when one was using the exploratory arc as the shot point one took shot points along that and measured on the datum arc, and one took the shot point not merely in the middle of the exploratory arc, but at the end of the arc as well, because, if only the middle point of the exploratory arc was taken, nothing would be tested but the behaviour at the middle of the arc. One was not justified in going the other way round, and concluding anything except that one was running along an arc and something might happen.

His colleague, Dr. Shaw, and he had under consideration the possibility of employing Dr. Jones' seismograph on a practical proposition as a reflecting instrument. The situation was that a certain amount of work had been done in the field and certain results had been obtained, but those results were not quite so clear as they should be, because, unfortunately, although one got instances of people hitting limestone when there was nothing but sand and then a nice little slab of limestone at the bottom, separated neatly, as it were, in actual fact the sedimentation rocks deposited themselves in a series of slabs in most places, and there was a lack of homogeneity in the depth profile, whereby the interface did not always show up as one hoped it would do. Something intervened; a blanket had been put there, and that was the thing that showed up. That appeared to have happened in the case of the refraction shooting; there was a blanket layer which one did not want at all.

In view of the tests which it was proposed to carry out, he was particularly interested in what was being done to test the capacity of Dr. Jones' seismometer, which was designed as a refraction seismometer, to do reflection work, and he felt with Dr. Rankine that there was a certain amount of doubt as to the significance of the test. He noticed in the time-distance records there was a good deal of variation in the slopes of the lines, and, although the velocity corresponding to one slope was given, it was obvious, by looking at the diagram, that there were varying velocities involved. In Fig. 3a, for instance, the slope of the bottom graph was very much less than the slope of the top graph. He did not know what the actual differentiation would amount to in velocities. The same thing occurred to a certain extent in Fig. 3b, where there was a con-

siderable variation in the slope of the two graphs at the top. It must be remembered that in all the slopes a slight change in the angle made a considerable difference in the speed. With regard to Fig. 3c, he was not quite clear as to how the nine graphs shown there were obtained. Were they successive peaks in one seismograph?

DR. JONES said that was so.

MR. LANCASTER JONES, continuing, said he thought the method was very ingenious, but the trouble was that one knew what one was after, and carefully designed one's conditions as a test to get it, and therefore one could look at the combination record, Fig. 2c, and, knowing what one did from Fig. 2a and Fig. 2b, one could plot the little kink that was taken as the significant feature. He was intensely interested in the subject, however, and would like more tests of the same kind designed to ensure that the particular seismometer in question could be used for reflection shooting. It would be exceedingly valuable if that was proved to be the case. The ordinary instrument sold for reflection shooting cost about £3000, which was a good deal to pay for something which might or might not be of use. Reflection shooting appeared to be all the vogue now; everybody who came from America said: "It is no good doing refraction shooting; it is out of date by ten years; do reflection shooting." Therefore it would be very useful if a simple instrument could be obtained to do reflection shooting.

PROFESSOR O. T. JONES said that, like previous speakers in the discussion, he had been interested in the method of determining the surface by reflection, and he had hoped that Dr. Jones had solved the problem, but he was a little disappointed in the results. If one had started a charge of 55 lbs., say, at the surface, that would not be quite as much as 55 lbs. at the reflecting surface, and it would be less than the equivalent of 55 lbs. when it came back again, but he found that Dr. Jones had had to use three or four times 55 lbs. to get anything recognizable at the recording point. Did not that rather indicate that the 55 lbs. had gone down on to the reflecting surface? One would not detect it at the point where it met the direct wave. It seemed to him that the result was to show that 55 lbs. was not sufficient to produce a reflection from any surface, according to the data given.

Another point which had occurred to him was that it was not quite the same thing shooting from O and shooting from I, unless the materials near the surface—the surface deposits, whatever they were—were the same. Supposing in one case there was nothing, and in the other case there was 50 ft. of gravel; the wave in going through that superficial material would be very much slower than in going through a solid material. Therefore the difference in that respect would make a considerable difference in the time of travel away from O and away from I.

He would like to have some assurance on the points he had mentioned.

MR. E. S. L. BEALE said he had thought of asking Dr. Jones how much faith was required in interpreting these seismograms, but he would not

actually ask him that. It did occur to him, however, in looking at the diagrams, that it was a little difficult for anyone without a great deal of experience to pick out the points in question, and he thought it would be an advantage if there was some method whereby it could be made more easy to do so. What struck him about the curves was that what was actually being picked out on the diagram (taking, for instance, the top one in Fig. 2c) was quite a sharp kink. That seemed to be the characteristic which was being looked for—a sharp kink. The analysis of curves of the kind in question was quite well understood in communication engineering, and it was quite well known that a sharp change of direction in a wave was represented by high-frequency components and could be produced only by high-frequency components. It was not possible in any circumstances to combine two, three, four or any number of continuous low-frequency waves so as to produce a sharp kink.

If one had two waves, both of low frequency but of somewhat different amplitude and/or frequency and phase, and added them together, one might think there would be a kink, for instance at their intersection, but it was not possible in fact to get a kink in that way. It was known that it must be represented by high frequencies. It was also quite well known that one could eliminate low-frequency components in a wave by means of filter circuits. It was rather more difficult and the theory was more complicated if one had to deal with a non-recurrent wave form—something which happened only once—but still quite a useful degree of separation could be made.

Taking a wave form of the shape which was shown in the top diagram of Fig. 2c (at the point marked by the arrows), the point being looked for was marked by the first arrow. If a wave of this form was put through a filter, it could be separated into two (or more) low-frequency waves, but, in addition to that, there was something *here* (at kink in the wave at the first arrow) which was made up of components of very much higher frequencies. The low frequencies could be eliminated by a simple low-pass filter leaving only the higher frequencies.

In other words, the kink would be left behind after all the low frequencies had been eliminated. It had occurred to him that something of that sort might simplify a great deal the finding of the points in question and be a little less subject to doubt. It was very much more easy to do it in the case of an electrical device, because one could rig up the required filter circuits without difficulty; but nevertheless there was a perfectly good analogy between mechanical and electrical systems, and it might quite well be possible to produce a mechanical device which would answer the same purpose.

MR. GEO. C. MCGHEE said he was certain that everyone would agree with him that Dr. Jones had presented a very ingenious method for directly simulating all of the time relationships involved in the reflection of sound from a horizontal plane surface. He agreed with Dr. Jones that the phase velocity of the reflected wave pulse along the horizontal surface offered the most important criterion for the dissociation of this pulse from the others appearing on the record. It was thought, though, that the demonstration could have been made more effective if Dr. Jones had, as

is the current practice, placed his instruments closer to the hole than was necessary to obtain reflections at the critical angle or disposed them symmetrically with respect to the hole. As Dr. Jones has indicated, sufficient reflected energy is available at vanishingly small angles of incidence despite theoretical considerations from classical elasticity to the contrary. Such procedure is recommended for ordinary dip practice by the fact that an error in dip determination due to an incorrect velocity assumption decreases with decrease in the distance of the receiving instruments from the hole, attaining a minimum for symmetrical disposition, and by the fact that Dr. Jones would have been freed from the limitation of being able to apply his method only to reflections from formations possessing a high wave velocity. In the experiment described this would have necessitated placing the instruments closer to or symmetrical with the point O. This would have resulted in a higher phase velocity for the reflected wave along the horizontal surface, infinite for the case of symmetricality, and would have made the velocity a more valuable criterion for dissociating the quasi reflections from the refracted events. In Fig. 3c this would have been evidenced by a greater difference in angle between the line drawn through the quasi-reflections and that through the refractions.

Dr. J. H. Jones, in replying to the discussion, said he was sorry Professor Rankine could not agree with him about the results of the experiment. He thought that if Professor Rankine would devote a day or two to the study of the seismograms he would change his views. He himself had spent a considerable amount of time with these seismograms, and believed that the result was quite genuine; he made doubly sure of it by measuring the time of the first peak in the quasi-reflection movement, and that certainly agreed well with the known facts.

With regard to Mr. Lancaster Jones' question as to the necessity of the datum arc, the usual practice was to supplement the arc information with that from a linear traverse which determines the velocity of the wave through the formation. In the present case it had been considered unnecessary to determine the wave velocity as the desired information could be obtained from the datum arc. If the correct picture could be obtained from the datum arc, then one would be certain that the wave had penetrated to the rock at the exploration end. That was the reason for the datum arc.

Professor Jones had asked a question about the size of the charges. Fifty-five pounds was first tried at I, but the seismographs were not readable. One hundred pounds gave the same intensity at the seismograph as 55 lbs. alone at O, and when 55 lbs. at O and 100 lbs. at I were fired simultaneously, he believed he could see the effect of the 100 lbs. at I in the compound seismogram.

Another point which had been raised was the amount of energy in the reflected wave. Recently he had been using the American method which Mr. McGhee had just mentioned, and it had been found that very often the energy in the reflected pulse was actually greater than that in the direct pulse. He thought that was an extraordinary result, but it seemed to be true. There were no filters used in his recent work, so that there was no question of preferential treatment of the reflected pulse.

# EXPLORATION BY THE REFLECTION SEISMOGRAPH IN THE GULF COAST OF TEXAS AND LOUISIANA.

By E. E. Rosaire.*

## Introduction.

Geophysical methods of exploration were first proved of commercial importance, in the United States at least, in the Gulf Coast in 1923 and 1924. Since that time, this region has been one of the most important proving grounds for geophysical methods of exploration for petroleum. In spite of the successful introduction of geophysical methods of exploration into other petroleum-producing provinces, and the consequent distribution of geophysical laboratories and shops, the volume of geophysical exploration and research is greater in the Gulf Coast than in any other petroleum-producing province. Obviously, an inspection of the reflection seismograph, as operated in this territory, should be of more than passing importance.

## Historical.

This method, as initiated and developed into a field-worthy mode of exploration, by the Geophysical Research Corporation, was first tried out in the Gulf Coast in 1926, perfected in Oklahoma during 1927 and 1928, and then re-introduced into the Gulf Coasts of Texas and Louisiana in 1929 and 1930. In this re-introduction,[1] the initial attempt to use the same methods of correlation of reflections from shot point to shot point, as developed and successfully used in Oklahoma, was tried and discarded because of the apparent absence of obviously correlatable reflections. Shortly thereafter, however, in a reflection seismograph survey of the marginal prospect, indicated by the torsion balance and refraction seismograph prospect near Darrow, La., the idea of mapping subsurface structure, by the buried dips shown by the step-outs of the reflections on the individual traces, was conceived and immediately developed into a practical field method.[2]

The introduction and growth of this method are shown chronologically in Fig. 1, together with the corresponding activities in torsion balance and refraction seismograph exploration, as well as an index of the price of oil. In 1929 and 1930 exploration was reduced to a minimum in this province. Although this decrease of exploration was primarily due to the rather general recognition that the two standard exploration methods, the torsion balance and refraction seismograph, were yielding only marginal and sub-marginal prospects, the practical cessation resulted from a flood of low-priced petroleum from the vast East Texas oil-field. In late 1930

* President, Independent Exploration Company, Houston, Texas.

and 1931, however, the recognition of Conroe as a major oil-field initiated a definite immigration of Mid-Continent oil operators into this territory. Since they were well acquainted with the excellent performance of the reflection seismograph method in the Mid-Continent, as used by the

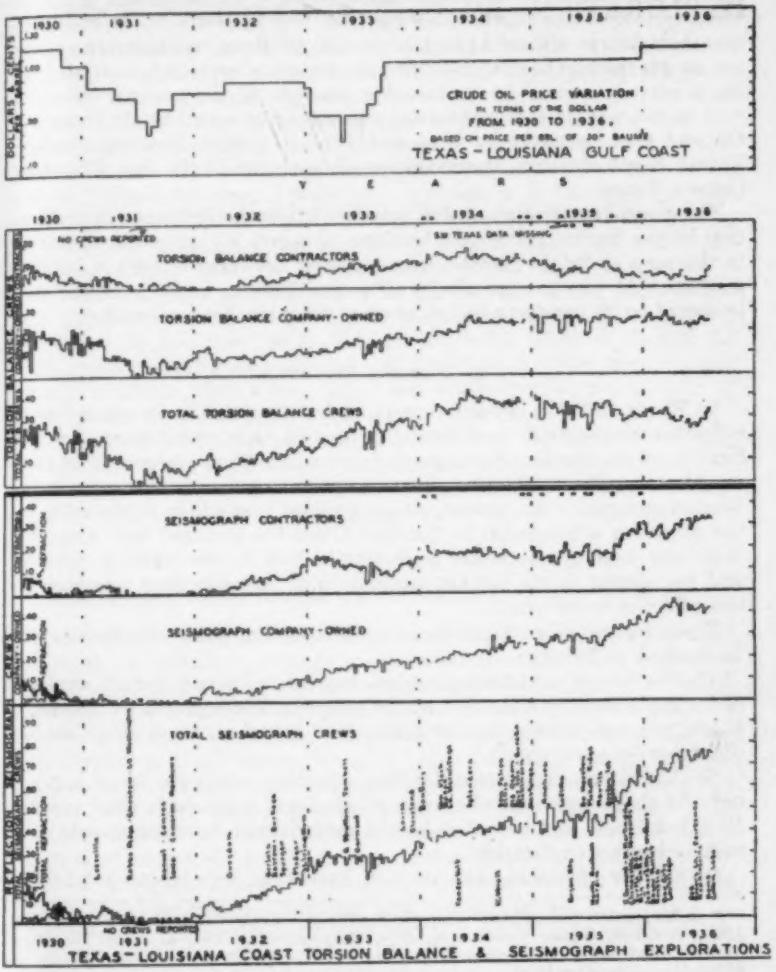



FIG. 1.

Geophysical Research Corporation, these operators were quite willing to use the reflection seismograph in the exploration of the Gulf Coast. Some of the local operators, such as the Humble Oil and Refining Company, had also initiated reflection seismograph exploration in this area for their

own account. It is interesting also to note how the increased activity in exploration by the reflection seismograph in this area coincides with the increase in the price of oil from 1930 to 1932.[3]

Since most prospectors like to have some definite excuse for drilling a wildcat well, the use of the reflection seismograph to examine old prospects was the natural procedure. However, the finding power of the reflection seismograph was utilized to best advantage by those operators who made use of this method to evaluate marginal prospects previously indicated by the torsion balance. An outstanding example of the rewards following such tactics was the string of three consecutive hits scored by the Stanolind Oil and Gas Company in 1934 and 1935 (Hastings, Brazoria County, Texas; South Houston, Harris County, Texas; and Turtle Bay, Chambers County, Texas).

The general recognition of that principle led to the last stage of exploration by the torsion balance, in the form of a race by the major operators in this area to be the first to complete their networks of torsion balance stations. At present, practically all torsion balance activity in this area is carried on by company-owned crews making blanket exploration.

## The Present Situation.

In March 1935 the prediction was made [4] that the major operators of reflection seismograph exploration parties in this province soon would have so much reflection seismograph data on individual prospects that they would, naturally, start tying these prospects together in order to secure blanket coverage. At present, an appreciable part of the exploration by the reflection seismograph in the Gulf Coast has assumed that form, for more and more operators are neglecting to look for prospects to explore, and are turning to the blanket exploration of township after township by the reflection seismograph.

From the use of such tactics at least three important conclusions can be reached, as follows:

(*a*) The law of diminishing returns has run its course for all methods of finding power less than that of the reflection seismograph, so that there is less and less justification for exploration by any method available but the reflection seismograph.*

(*b*) Additional exploration by the reflection seismograph is justified only for those operators who have accumulated appreciable areal surveys by this method, and who thus have a material patchwork upon which to make a blanket exploration.

(*c*) Smaller operators, who do not have this prerequisite patchwork,

* In his presidential address before the Society of Petroleum Geophysicists, Mar. 24, 1933, Houston, Texas (*Trans. Soc. Petr. Geophysicists*, 1933, **4**, 3–12), Mr. Paul Weaver used the term "resolving power" to indicate the theoretical difficulty of obtaining information by the "potential function methods" of geophysical exploration (gravitational, magnetic and electrical methods). There has been an extension of the use of the term "resolving power" to all methods to indicate the "ability to make obvious" the remaining undiscovered oil-fields. In a recent conversation with the writer, Dr. L. W. Blau, of the Humble Oil and Refining Company, Houston, Texas, suggested that the term "finding power" would be more descriptive and proper, and so the "finding power" of a method is used in this article to indicate the "ability to make obvious oil deposits as yet unproved by the drill."

are not justified in exploration or prospecting in this area until a method of still higher finding power is made available.

As is usually the case, the prospects being turned up by this blanket exploration are, quite generally, the less obvious ones, and ones which, from the standpoint of relative relief, would have been considered as marginal two or three years ago. While some of these less obvious prospects have been indicated as potential oil-fields of importance by development, the greater number have been found disappointing upon development, indicating relatively small accumulations of oil, or, even worse, no commercial production even after several wells have been drilled.

The failure to find oil on these structures of low relief may not be conclusive, because of the faulting, often quite complicated, associated with each Gulf Coast structure. Since good correlations in this area are more nearly the exception than the rule, analyses of these fault systems by using the reflection seismograph are expensive, tedious, and often unreliable. Since the disinclination to continue development until production is established increases progressively with the number of dry holes drilled on a prospect, the woods are full of geophysical prospects apparently condemned by one, two, or even three dry holes, while the search for virgin prospects continues unabated. If a method of higher finding power is made available, then these, tested and so far dry, structures will, of course, be the first-class prospects of another new era.

Although the method under discussion is no longer the bright and shining example that it was in 1934 and 1935, a review of the developments which resulted from the use of the reflection seismograph, as well as the developments in the method itself, should be important as well as interesting.

## Developments Resulting from the Use of the Method.

At the time that the method was first introduced, there were prevalent several misconceptions regarding the subsurface situation which have since been dispelled in accordance with confirmations of the predictions which followed the use of the reflection seismograph. Thus, in 1930, the sedimentary structure around a salt dome was generally supposed to be much like the wood fibres near a nail driven through a plank; faulting, though reported occasionally in the literature, was regarded as unusual, and certainly not regional; the sedimentary structure of the Gulf Coast was assumed to be a heterogeneous accumulation of lensing sands and shales; the subsurface structure of known fields like Orange, Goose Creek and Welsh was unknown, and the possibilities of production from structures like the Tepetate oil-field, in Acadia Parish, Louisiana, were not anticipated.

Six years later, with the number of reflection seismograph crews operating in the area increased to seventy, the following developments can be directly attributed to the use of the reflection seismograph.

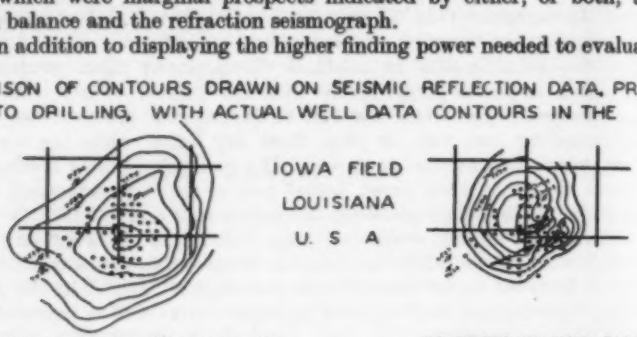
1. *Better definition of marginal and sub-marginal prospects previously indicated by the torsion balance and refraction seismograph.* The first confirmation of the predictions of this method was made by the Vacuum Oil Company[5] in the B. T. Waite No. 1, at the Iowa oil-field, Calcsieu Parish, Louisiana, on October 22, 1931. The analysis of this

area, a prospect previously indicated as marginal by the torsion balance and refraction seismograph, was made by the use of accumulated plotted dips, and is shown in Fig. 2A, with interpretation of the subsurface, as now postulated, shown in Fig. 2B.

The discovery of oil in a structure of this type naturally stimulated the search for others, generally called "Iowa" types of subsurface structure. Shortly thereafter this method was used on those (non-geophysically predicted) oil-fields like Goose Creek, Welch, Orange and Houma which had formerly been called "non salt dome" oil-fields. These were all found to be typical "Iowa" types of structure. Examples of other "Iowa" types of structure, later indicated as such as a result of the use of the reflection method, are Anahuac, Hastings, Bosco, Turtle Bay, and La Fitte, all of which were marginal prospects indicated by either, or both, the torsion balance and the refraction seismograph.

So, in addition to displaying the higher finding power needed to evaluate

COMPARISON OF CONTOURS DRAWN ON SEISMIC REFLECTION DATA, PRIOR TO DRILLING, WITH ACTUAL WELL DATA CONTOURS IN THE




CONTOURED ON SEISMIC REFLECTION DATA PRIOR TO DEVELOPMENT
2-A

CONTOURED ON WELL DATA ON HETEROSTEGINA SAND
2-B

the marginal and sub-marginal prospects previously indicated by the torsion balance and the reflection seismograph, this method also served to first definitely classify these anomalous "non salt dome" oil-fields discovered in the pre-geophysical days.

2. *Prediction of Occasional Marked Uniformity in Gulf Coast Sedimentation.* During 1929, 1930 and 1931, some geologists, and some geophysicists, admitted the possibility of getting reflections in the "hard rock" country where alternate bands of shales, sands and limestones occurred, but refused to admit the possibility of getting reflections from the Gulf Coast sediments, where reflecting horizons similar to the Viola Limestone and the Austin Chalk had not been indicated by the drill. In addition, many more geologists and geophysicists refused to admit the possibility of correlation of reflections in the Gulf Coast, where the sedimentation was supposed to be, laterally, anything but homogeneous. Naturally, there was little credence given to the thesis that correlation of reflections from shot point to shot point was occasionally possible.

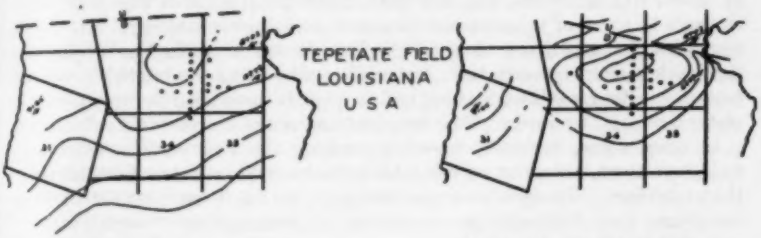
The brilliant success of the Schlumberger method of electrical logging in the Gulf Coast confirmed this earlier prediction by the reflection seismograph. In fact, after this was established, many of those who had previously come to scoff, remained to pray, and also to sway to the other

extreme; namely, that much more correlation was possible than even the earlier proponents of correlation had believed.

3. *Prediction of Faulting in the Gulf Coast Structures.* Prior to the introduction of the reflection seismograph into this province, the possibility of faulting, although occasionally recognized and recorded in the literature,[6] was not generally accepted. A rather prevalent idea was that the Gulf Coast sediments would bend and not break under the stresses and deformations involved in the formation of salt domes.

However, shortly after the introduction of the method, and during the period when the dip method of exploration was generally relied upon, closed dip traverses were frequently found which failed to close by appreciable amounts. In March 1933 [7] the writer suggested the use of the word "mis-closures" for such large errors in closing, and also suggested that such mis-closures were due to the presence of material faulting in these Gulf Coast structures. With the introduction of the better well correlation resulting from the Schlumberger method of electrical logging, the presence

COMPARISON OF CONTOURS DRAWN ON SEISMIC REFLECTION DATA, PRIOR TO DRILLING, WITH ACTUAL WELL DATA CONTOURS IN THE




CONTOURED ON SEISMIC REFLECTION DATA
3 - A

CONTOURED ON PRODUCING SAND
3 - B

of such types of faulting was later demonstrated, and found to be, quite frequently, of material commercial importance.

4. *Focusing of Attention upon the "Tepetate" Type of Structure.* The "Tepetate" type of structure has been so named from the field of that name found in August 1935 by the Continental Oil Company in their No. 1 Vincent in Acadia Parish, Louisiana. It is best described as an oil-field in which accumulation is primarily due to the closure produced on a flat nose by a fault downthrown down the regional dip, as shown in Fig. 3A. This interpretation of the structure was made by correlations from a reflection seismograph survey, before oil was produced, and later confirmed by electrical logging in subsequent wells, Fig. 3B. At least one other type of field had been found prior to the recognition of this kind of accumulation at the Tepetate Field, the Louise Field in Wharton County, Texas. Other fields in the Gulf Coast now generally recognized as of that type are Hamman and Eureka. Two additional prospects of this same type are now being tested by the drill. Localities where this type of structure is important are those where regionally high wells are dry, and regionally low wells produce oil.

5. *Prediction of Regional Faulting.* As soon as the general characteristics of the "Tepetate" type of structure were recognized, operators of reflection seismograph crews, recognizing that similar anomalies had been found east and west of the "Tepetate" Field, started a detailed examination of that trend. As a result, several similar anomalies have been found along a regional strike fault extending for a distance of approximately 100 miles east and west. This fault system is uniformly downthrown to the south with throws varying from 100 to as much as 600 feet. There are several other suggestions of such regional faults, and in each case the indication is that the faulting is downthrown down the regional dip.

## Developments in the Method.

Since 1929, when the method was first introduced on a commercial scale in the Gulf Coast, definite improvements have been made in interpretation methods, field methods and apparatus, discussed below as follows:

1. *Interpretation Methods.* The possibility of using dips, as calculated from the step-outs on the records, was first recognized in the Gulf Coast in 1929. One very important development of this method was the use of closed dip traverses, and the postulation that some of the large misclosures in some of these closed traverses was due to faulting. The location, direction and throw of such "dip" faults are recognized to be qualitative rather than quantitative, but such analyses have always proved at least interesting and illuminating, and frequently have been the only possible method of attack because of the frequent absence of correlatable reflections.

In some areas, however, where apparently the Frio sand is thick and well developed, excellent correlatable reflections have been obtained from that interface. In such and similar cases, it has been possible to map structure and indicate the existence of faulting on "correlatably" reflecting horizons.

An outstanding development was that, in the case of some exploration of faulting on such horizons, the presence of double reflections near the location of the fault were so well developed that their existence was laid to reverse faulting (repetition of section) rather than to diffraction, the correct explanation (for as a result of drilling through such faults, short rather than long sections were found).

2. *Field Methods.* In the early stages of reflection exploration in this province, the quality of recording apparatus varied considerably, for some of the operators relied entirely upon shallow hand-dug shot-holes, while others had to rely upon deeper machine-dug shot-holes, required in order to eliminate the undesirable surface waves. However, with the depth of drilling increasing to nearly 12,000 feet, and the resulting need for deeper exploration, the use of machine-dug shot-holes has become almost general.

One interesting development in shot-hole drilling has been that of jetting shot-holes in swampy and marshy areas by the use of water-jets from portable gasoline-engine (outboard motor) driven centrifugal pumps.

With this definite trend towards the use of deeper shot-holes, one of the dynamite manufacturers [8] directed attention to the probability that the dynamite generally used was not exploding properly at the depths and pressures involved. By the introduction of a special dynamite, the average

size of the charges has decreased, with resulting better-quality records and practical elimination of misfires.

The need for accurate "time breaks," or shot instant recording, has led to a definite improvement in the quality of the electric caps available.[9] Those now furnished to this industry are remarkably uniform, and have much more desirable characteristics than those formerly available.

An interesting development in field methods has come about in the use, by about half of the operators, of composite or multiple recording.

The possibility of using the directional transmission employed successfully in commercial radiotelegraphy had occurred quite early to the members of the Geophysical Research Corporation staff. Dr. F. M. Kannenstine, then in charge of their laboratory, suggested such a possibility in 1927, and made some field experiments to see if such possibilities were real. His attention was primarily focused on the possibility of using charges distributed either in space or time. At that time, however, he was unable to observe any improvements which could be attributed to the use of multiple shots. Shortly thereafter, Mr. E. G. Taylor secured U.S. Patent No. 1,799,398 for a method of multiple recording in which he had hoped to accomplish the same end. This patent was purchased by the Geophysical Service, Incorporated, in 1930, and from that they have developed a system of so-called "composite recording."

Although the Taylor patent was primarily directed at the use of geophones disposed along half-wave positions, in order to eliminate the refracted wave, the developments made by the G.S.I., and copied by several other field operators, have been in the direction of using a large number of geophones located on the surface of the ground, and generally more or less inter-connected. They claim that thereby they are able to make a directional reception of the reflected wave. At present, the operators are equally divided in regard to their favouring this method of reception. It is a little difficult to understand why, with physicists capable of developing these methods and making successful interpretations of the results, such a dispute should continue to rage for several years. When the physicists, so called, who are in dispute as to the merits of this method are unable to agree, the diverse opinions of the geologists concerned in the use of these methods is no more difficult to understand.[10]

A modification of this attempt at directional reception has recently appeared on the scene. This modification has been described by Mr. Frank Rieber.[11] The method which he has developed is most interesting. Instead of recording the seismograph impulses on a strip of sensitized paper by the usual galvanometers, he records the seismograph impulses on a film in the same manner that sound-tracks are made for talking motion-pictures, and so secures a seismograph record which is repeatable, and is also subject to mechanical analysis. Mr. Rieber combines the impulses from ten or more seismographs distributed over the surface of the earth, each recording on an individual sound film, into one composite record. This he does by scanning the individual strips in accordance with possible angles of emergence throughout nearly 180 degrees. At given angles of emergence, particular reflections are best developed. Thereby, he claims to secure a definite improvement in directional reception. He calls his method "Controlled Directional Sensitivity," and alleges that this method

of reception and analysis is utilized to the greatest advantage in the exploration of highly folded and faulted structures. Although actual results of his new method are not available, this development will be watched with great interest by all interested in the future development of the art. It is obvious that there is a possibility that this method originated by Rieber will combine the advantages of both the recording methods now in dispute. The fundamental objection to the composite method of receiving is that thereby the impulses are scrambled before they are recorded. However, Rieber first records his impulses and then later scrambles them at will.

Material improvements in the apparatus have taken place in the equipment used here, as in other parts of the United States. There are three definite improvements as follows:

1. Machine Cranking.
2. Volume Control.
3. Elimination of Oil for Damping.

These will be taken up in order below.

1. *Machine Cranking.* The introduction of machine cranking in taking the records was made in an effort to assist the interpreters in correlation work. The first field oscillographs were cranked by hand. However, when this hand-cranking was replaced by machine-cranking, either in the form of a spring motor or an electric motor, correlation was materially facilitated, because the distribution of timing lines along the records was made much more uniform, and similar times on different records could be compared directly. Variations in arrival times of similar reflections were made much more obvious. Also, the opportunity to compare the quality of individual reflections was facilitated, because then a given reflection impulse always occupied the same space on a record.

2. *Volume Control.* In the case of the first reflection records taken, they usually started off with a maximum amplitude immediately after the first arrival, decreasing to ground static level at the end of the record. As a result, there was only a limited part of the record in which the amplitude was neither too great nor too small to be useful. Preliminary attempts at controlling the volume of these recorded amplitudes were made by those operators who favoured the use of string galvanometers. In order to keep these strings from overlapping during the early stages of this great amplitude, the amplitude of the string vibration was controlled by a rheostat, operated manually, connected across the strings. This method, however, had only two positions, and so the "volume control" was not uniform. As a substitute for this, a semi-automatic volume control was later introduced which made it possible to keep the amplitude on the record readable at all times. There is one rather strong objection to the use of such types of semi-automatic volume controls. When these are used, the first breaks, which are of greatest importance in making corrections for the surface low-velocity layer, are generally non-existent, or of an amplitude so low that they cannot be accurately read, and as a result the corrections for this low-velocity surface layer are made much less reliable.

3. *Elimination of Oil for Damping.* As a general rule, most of the

geophones or seismographs used in the early reflection recording were oil-damped. Since year-round variations in field temperatures of 100° F. are not at all uncommon, and all the oils in general use have marked temperature coefficients of viscosity, there is an obvious objection to such methods of damping. If one type of oil were used throughout the year, the geophones were extremely insensitive in winter, but satisfactorily sensitive in summer. What generally happened was that when winter arrived, the observer would replace the oil which he had used in his geophone with a much lighter grade of oil. Then during the winter he got satisfactory sensitivity and satisfactory damping. However, with the advent of summer, he was, of course, not averse to the apparent increase in sensitivity which the geophones exhibited. In fact, he was rarely conscious of the increase in sensitivity, and so, in summer, while the dynamite charges went down, the quality of the records also went down. This decrease in quality occurred because the geophones were not satisfactorily damped in the higher operating temperatures in summer. Some of the operators have gone over to the use of either air-damping or electromagnetic damping for their geophones. The construction of such field-worthy geophones has been a definite contribution to field practice.

## The Future.

At this point, a *résumé* of the fundamentals of prospecting strategy may be appropriate. The basic theorems are as follows:

I. Discovery at a premium can be expected to follow from :—

A. *The Use of a New Method with Higher Finding Power in an Old Area.* Example: The introduction of the reflection seismograph into the Gulf Coast in 1929, which by virtue of its higher finding power was able to convert marginal and submarginal prospects of the preceding methods, the torsion balance and the refraction seismograph, into the oil-fields of Hastings, Anahuac, La Fitte and others.

B. *The Use of an Old Method in a New Area.* Example: The use of the refraction seismograph in the lakes and bays of South Louisiana in 1927 and 1928, as a result of which eleven salt domes were discovered in nine months, the highest rate of finding ever experienced in this area.

C. *The Use of an Old Method in an Old Area, but with a New Objective.* Example: The use of the reflection seismograph method in the East Texas Syncline with structure on the Georgetown Limestone as an objective. Although the area had been properly explored by the same method on the Pecan Gap Chalk and the Austin Chalk, at least two new fields, Cayuga and Long Lake, have been found since, for over those structures there is material closure on the Georgetown, and little if any on the Austin and Pecan Gap Chalks.

D. For an exploration campaign [12] rather than for a prospecting sortie, discovery at a premium in a given area, can be expected to follow from:

1. The discovery of prospects by the appropriate method of lowest operating cost, and the evaluation and culling of these prospects by the successive use of the appropriate methods of higher finding power (successive high grading).

2. Prospect development in a particular area should not be initiated by any given method until the area has been explored by the appropriate methods of lower cost.

Example: The most successful operator of the reflection seismograph in the Gulf Coast to date is the Stanolind Oil and Gas Company, who steadfastly adhered to the policy of locating prospects by the torsion balance and evaluating then by the reflection seismograph.

3. An apparent exception to this rule is the early use of the reflection seismograph recently proposed [13] in the evaluation of sedimentary thicknesses when such data are not available from wells.

Example: The prediction, by the reflection seismograph, that the sedimentaries were only 2800 feet thick on the Chadron Uplift in Northwestern Nebraska, but more than 7000 feet thick in South-western Nebraska, before any such information was available from wells.

II. The introduction of a method of higher finding power immediately raises the potential value of the marginal and submarginal prospects remaining from the previous methods of lower finding power, and therefore a renaissance of the former methods is possible and often desirable, for thereby prospects can usually be found cheaper than they can be discovered by a blanket exploration with the new method. With the arrival upon the scene of a new method of higher finding power, foresighted operators will seize every opportunity to complete their libraries of data resulting from the use of the methods of lower finding powers, even though that means the acquisition and purchase of negative data.

Example: The introduction of the reflection seismograph into the Gulf Coast put a premium upon torsion balance and refraction seismograph data in the area. Several foresighted operators took every opportunity to complete their torsion balance networks by the acquisition and purchase of negative data previously secured by other operators.

## Conclusions.

With these rules in mind, a reasonable expectation is that, unless a method of higher finding power appears upon this scene, the present activity in reflection exploration should decline materially in the future. If such a method should appear within the next six months, the decline will be postponed until the major operators now using the method have completed their blanket explorations of the Gulf Coast. If the introduction of such a method is postponed for more than a year, then following such an introduction, there will be a smaller secondary peak in the reflection seismograph activity.

Simply because such predictions are logical, however, there is no reason to believe that they will come true. Activity in the method may continue unabated, as is the case in California at present. A rough estimate places the cost of the Old River Field (recently found there by the Shell Petroleum Corporation, following a reflection seismograph survey), to the industry in California of between ten and fifteen million dollars for reflection seismograph work alone. While there seems to be some effort to put this discovery into the class of I.C. above (old method, old area, but new objective, because of somewhat greater depth), still the state of affairs was evident

several years ago. If half that amount of money had been intelligently invested in the development of new methods of oil-finding, it is reasonable to believe that the California reserves in sight would be much greater now than they actually are.

Therefore, foresighted operators in the Gulf Coast will probably do two things:

1. Make intelligent investments in possible new methods of oil-finding with potential finding powers still higher than are available in the methods now in use.

2. Complete their blanket explorations of this area by the reflection seismograph in the shortest possible length of time and at the lowest possible cost. This means the purchase and acquisition of otherwise negative data already secured in this area by other operators. The completion, and proper interpretation, of such a blanket exploration should result in complete information as to all the possible marginal and submarginal prospects which can be found in this province by the reflection seismograph, which method has the highest finding power of any method used to date in this area on any intensive scale.

## Acknowledgments.

The writer wishes to express his indebtedness to Mr. H. C. Cortes, of the Magnolia Production Company, for helpful comments and other assistance, and also to Mr. O. L. Brace, who contributed the subsurface contours presented for the Iowa and the Tepetate Oil-fields.

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## *DISCUSSION.*

PROFESSOR V. C. ILLING said that he had personal experience of cases in which the amount of geological evidence available was extraordinarily small, and after the seismic survey it had been proved by drilling that the geological picture obtained by the reflection survey was substantially correct. As a geologist he would like to pay his tribute to what geophysicists had done. In his opinion reflection shooting was an extraordinarily useful tool in the elucidation of structures in sedimentary rocks. Mr. Rosaire's paper was of importance, he thought, in its development of the tactics of geophysical work.

MR. GEO. C. MCGHEE wished to express appreciation to Dr. Rosaire for this very valuable addendum to his previous historical studies of the exploration by the reflection seismograph in the Gulf Coast. As such it had more than local significance. Since the re-introduction of the method into the Gulf Coast in 1929 mentioned by Dr. Rosaire, it had been used almost exclusively in dip determination, and had not undergone any fundamental changes in technique, enjoying rather a gradual refinement that would permit the mapping of less pronounced structural features. Dr. Rosaire's index of progress in this respect as representing the difference in technique required to locate the "Iowa Type" and the "Tepetate Type" of structure is well founded. Although Iowa was a marginal torsion balance and refraction seismograph prospect, its very large structural uplift made it very easy to locate with the most casual dip survey. Preoccupied with the exploration for this type of structure, operators did a great deal of work during 1932 and 1933 which did not utilize to the fullest extent the seismograph's "finding power." Structures of the "Tepetate Type," including Tepetate itself, were shot without being correctly interpreted. When it is realized that this type, which may involve only 100 to 200 feet of structural closure at a depth of 6000 to 8000 feet, and which may have associated with it no dip greater than 300 feet per mile, can be mapped with a degree of accuracy approximating that of any subsurface method that could corroborate it, then does one appreciate the extent to which refinements have been introduced. An accuracy in dip of about 50 feet per mile, which represents an angle of approximately a half of a degree, can usually be attained. It should be pointed out that Dr. Rosaire takes a very independent view with regard to the value of correlations in the Gulf Coast. It was thought that the consensus of opinion among Gulf Coast operators was that correlations were rarely worth considering. This did, unfortunately, eliminate the possibility of locating faults except in such places where a decided change in dip occurred across the fault or where it was required from the dip relationships in a dip network running around the fault. If such an analysis was included in Dr. Rosaire's interpretation of "mis-closures," it was agreed that faults could on rare occasions be located. It would not seem, though, that the mere fact that a dip traverse had failed to close could be productive of much quantitative information.

PROFESSOR A. O. RANKINE said he had one suggestion to make, which he was afraid was a rather frivolous one. It would, however, briefly illustrate his feelings with regard to Dr. Rosaire's apparently high opinion of the reliability of the reflection method. Professor Illing already knew them very well.

As he had already indicated, he had grave doubts as to the possibility of picking out with reasonable certainty reflection onsets in a seismic record already highly agitated, and he felt that more was needed in the way of testing, perhaps by Dr. Jones' method or perhaps otherwise, to see whether real phenomena were, in fact, being observed.

He noticed in Dr. Rosaire's paper that money seemed to be a quite unimportant consideration; it was stated, for example, that about £3,000,000 had been spent in California on reflection seismic work in one field alone. He would suggest that some of the money available should be spent in building an artificial structure on which experiments could be carried out, with the assurance that one would really know what was underneath one's feet. He understood that recently the cost of erecting a ferro-concrete mountain had been worked out by the costing staff of the Metropolitan Vickers Company, and they had found that to build a 15,000-feet mountain in Sussex would cost, apart from the freehold of the site, £1,000,000,000. He was not suggesting anything quite so big as that, but perhaps several millions might be spent in constructing a series of underground beds and ascertaining by experiment whether in fact one could get at one point as many as twenty-two reflections, as he had seen claimed.

PROFESSOR V. C. ILLING, in replying to the discussion, said that he could only speak as a geologist who had some experience of what reflection seismic work could do. He was quite satisfied in his own mind that under suitable geological conditions the number of reflecting horizons did sometimes attain the order of fifteen to twenty. Nor, considering the small percentage of the total energy involved in a single reflection, did this seem surprising in view of the rapid changes in lithology. The proof of the method lay in what it had achieved, and no one conversant with the history of prospecting in the Mid-Continent over the last five years could doubt its ability to find and delineate geological structures under difficult conditions. When it came to the details of individual reflections, there was considerable room for differences of opinion and a considerable amount of reflection work in difficult country achieved results which were by no means clear and unchallengeable, but the large sums of money spent yearly in America on seismic work were largely contributed by the main oil companies, because they found that the policy paid. He was quite satisfied that reflection work was producing geological evidence which could not be obtained by any other known method.

If geophysicists in this country were still sceptical of what reflection work could achieve, the geologists of this country could show them many known structures on which they could test out the method. It would take both money and time, but the method was so important that it was worth a complete try out. Speaking from the geological point of view, he had no hesitation in saying that in the realm of exploratory work in

oilfields the positive result of a reflection survey was far more satisfying that the results of any other geophysical method. He did not deny the fact that the method was expensive, nor that it was unsuitable to all geological problems. No geophysical method was of universal application, each had its own particular sphere of usefulness; but it would be foolish to blind ourselves to the results already achieved because we were not prepared to go ahead with a method where there could be some difference of opinion as to the validity of individual reflections.

PROFESSOR V. C. ILLING then resumed the Chair, and, on his proposition, a hearty vote of thanks was accorded to the authors of the papers which had been presented.

*The meeting then terminated.*

DR. E. E. ROSAIRE, in reply, wrote: I was quite interested in finding that apparently some scepticism still exists, in England, as to the validity of the reflection results and the utility of the technique.

I am quite appreciative of Professor Illing's tribute to the usefulness of this method, and am interested in correlating his favourable opinion with his experience.

I am also gratified to Mr. McGhee for his appreciation, but beg to differ from him on a few minor points. Having supervised a material amount of reflection exploration in the Gulf Coast since the re-introduction of the method in 1929, I can assure him that for the last two years, during which time the bulk of the expenditure has been made for reflection exploration, the emphasis has been upon the use of correlations rather than dips, for the very good reason that by far the greater part of the structures remaining to be found and explored are those characterized by small relief at the depths which can be reached by the drill. Further, while he is correct in his statement that the structural uplift at Iowa makes it very easy to locate with "the most casual dip survey," he should remember that while such a task is easy and simple to-day, that same task was much harder at the time that the initial reflection exploration was made with experimental apparatus, with no previous experience, and in the face of general scepticism as to the validity of the method. He might as well comment upon the relative ease with which refraction exploration for shallow salt domes could be done as of to-day, while to discover and map such anomalies in 1924, 1925, and 1926 was quite a different matter. When a method becomes so well known and understood that the equipment can be built with the same ease that amateur radio operators now build wireless sets from parts bought by mail, discovery at a premium by that method is improbable. That is the existing situation in the Gulf Coast and Mid-Continent areas to-day.

Further, "the consensus of opinion among Gulf Coast operators—that correlations were rarely worth considering" is from one to three years out of date. I have tried to show that, in the use of an exploration method which passes, in a geological province as large as the Gulf Coast, from the introductory stage to near obsolescence in seven years, values and opinions as well as utility are subject to rapid change, and, as I said

above, for the past two years the emphasis has been upon correlations rather than dips. Further, I pointed out, in the third paragraph on p. 46, that "the location, direction and throw of such dip faults are recognized to be qualitative rather than quantitative," but I can assure him that in the hands of competent interpreters, such "dip" faults often have yielded clues and information of considerable value.

With regard to Professor A. O. Rankine's suggestion to make ferro-concrete mountains out of psychological molehills, such an exhaustive proof should hardly be of even academic interest now. The method passed out of that stage nine years ago. Further, I wish to point out that I did not say that the £3,000,000 had been spent in California in one

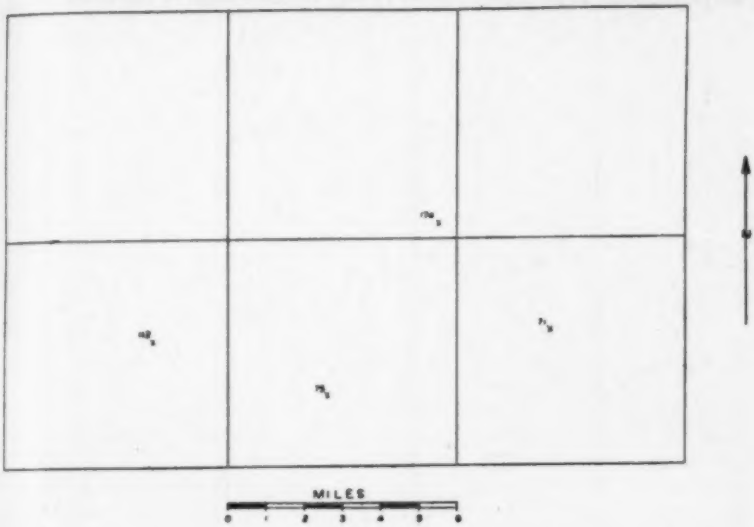


FIG. 4.

field alone. I arrived at that figure by estimating the cost of all the reflection exploration done in California prior to the discovery of the Ten Section (Old River) Field by that method. Neither did I have any intention to indicate that money was a quite unimportant consideration, for I am sure that equal or greater amounts of capital have been fruitlessly spent in other ventures wherein also hindsight later showed the expenditures might well have been avoided or diverted to better purpose. Further, while I have not yet seen a reflection record showing twenty-two reflections, I have seen many routine field records in which I certainly entertained no "grave doubts as to the possibility of picking out with reasonable certainty reflection onsets." Four such records, selected for their academic quality from a group of routine field records, are submitted herewith (Figs. 4 and 5). However, with the development of satisfactory volume-control apparatus, and with a thick sedimentary section like that which apparently exists in the Gulf Coast, I consider it well within the

realm of possibility that I may yet see what I would consider a satisfactory record showing twenty-two, and more, reflection onsets.

I quite agree with Professor Illing that the reflection method is expensive, and that it is not universally applicable. For instance, in perhaps one quarter of the State of Texas the method is not usable, because of the unfavourable, and as yet unsolved, effect of the thick limestone capping the Edwards Plateau. And yet, in spite of the fact that methods with potentially greater finding power are now in experimental use, it is my humble opinion that the reflection method will remain the most useful tool yet devised for geological (sedimentary) exploration, for of all the geophysical methods proved and now on trial, the reflection method, in its predictions, approximates most closely to the results of the drill.

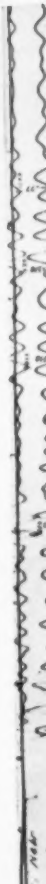

Fig 5.

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## TRINIDAD BRANCH.

### SIXTH ANNUAL DINNER.

THE Sixth Annual Dinner of the Trinidad Branch of the Institution of Petroleum Technologists was held at the Queen's Park Hotel, Port of Spain, on Saturday, November 7th, 1936, with Commander H. V. Lavington, R.N. (Branch Chairman), in the chair. The guest of honour was His Excellency the Governor, Sir Murchison Fletcher, K.C.M.G., C.B.E., who was attended by Capt. M. Godley, A.D.C. The following members and guests were present :—Capt. R. A. Adamson, Rev. F. R. Banks, Hon. A. E. V. Barton, C.B.E., P. Bayle, H. A. Bennett, R. G. Bennett, A. G. V. Berry, E. C. Buck, A. Chadwick, C. A. Child, K.C., R. F. Connock, W. G. C. Cooke, R. C. Cooper, W. G. Dale, L. G. Dalton, Major R. M. Decker, P. de Pass, L. A. A. de Verteuil, W. de Verteuil, S. G. Duncan, R. Edgeworth-Johnstone, A. Emlyn, Sir Geoffrey Evans, C.I.E., H. D. Fletcher, S. E. Folkes, W. N. Foster, Mr. Justice Gilchrist, R. Godfrey, G. W. Halse, H. A. Harris, Lt.-Col. the Hon. H. C. B. Hickling, D.S.O., M.C., C. Hobson, J. D. Hobson, K.C., L. C. C. Hobson, A. Humphries, R. L. Hunter, M.C., H. C. W. Johnston, Dr. Maxwell Johnstone, E. D. Kennedy, S. J. Kirton, J. W. Knights, W. D. Lambie, Capt. D. Lenegan, I. McCullum, J. H. McLea, A. R. McLean, J. W. Macgillivray, O.B.E., A. K. Mackenzie, Hon. R. S. Mackilligin, O.B.E., M.C., Dr. E. J. R. MacMahon, Col. the Hon. A. S. Mavrogordato, O.B.E., S. F. Mehling, F. L. Melvill, F. Middleton, C. A. Moon, F. Morton, J. Mowll, M. M. Nock, A. L. Owens, R. Palmer, C. A. Palmer-Chizzola, G. C. Pantin, A. Pickles-Pierse, A. R. Piotte, E. S. Pirie, M. R. M. Porter, J. B. Preston, E. G. D. Pritchett, H. O. Robson, H. W. Reid, R. Ring, J. T. T. Robinson, A. J. Ruthven-Murray, E. C. Scott, M.C., G. H. Scott, T. H. Scott, O.B.E., Hon. A. W. Seymour, C.M.G., V.D., Major G. H. Simpson, M.B.E., A. W. Slatter, D. Smith, Capt. A. C. Smith, M.C., Major T. Spence, E. G. Stibbs, A. Storey, D.F.C., C. Swabey, Lt.-Col. A. G. Tanner, D.S.O., M.C., H. C. H. Thomas, S. J. Voss, G. A. Walling, D. M. Walsh, B. W. West, C. C. Wilson, C. E. Wilson, H. Wilson, F. K. Worsley, Hon. E. J. Wortley, C.M.G.

#### "THE INSTITUTION OF PETROLEUM TECHNOLOGISTS."

After the toast of "The King," **His Excellency the Governor,** proposed the toast of "The Institution of Petroleum Technologists," and said : From the point of view of the Government, I welcome the presence in Trinidad of your branch of the Institution of Petroleum Technologists. I regard it of great value that we have a body of experts to whom we can turn for corporate advice, and there is a matter which I would wish to refer to their serious consideration.

The nations to-day move upon machines, and machines move upon oil. The Empire is unfortunately not self-contained in the matter of oil, and it has to rely upon foreign aid. In the event of war it is possible that, by reason of neutrality legislation or otherwise, that aid will be largely with-

drawn. England, realizing the position, is taking steps to distil petrol from coal. It is a very expensive process, requiring large capital. That capital is safeguarded by protection. I believe it to be the case that the production of 100,000 tons of petrol involves the United Kingdom taxpayer in a loss of revenue of some £1,000,000. But in spite of these steps which England is taking, it still remains necessary for her to import large supplies of oil from overseas. It is conceivable that in time of war oil imported from Trinidad may prove to be a most important factor, possibly a vital factor, in maintaining the safety of the United Kingdom.

Those far-sighted men who are exploring the resources of Trinidad have it in contemplation to open up undersea areas, for which purpose much new capital is required. But there is the difficulty of finding an assured market. We formerly sold oil in the United States of America, but in 1932 the erection of a high tariff wall closed that market to us. England buys a large quantity of oil from the United States. I venture, Sir, to hope that it may be found feasible to extend some measure of protection to Trinidad oil in the United Kingdom, in order that we may obtain there an assured market. To the taxpayer in the United Kingdom I suggest that such protection would be to him a form of insurance, the cost of which would be a mere bagatelle in comparison with the cost of other forms of national defence which England is being compelled to finance.

The Chairman, **Commander H. V. Lavington,** R.N., in responding to the toast, said :

I have pleasure in reading the following telegram which has been received from the President of our Parent Institution :—

> "Greetings from Parent Institution and best wishes for enjoyable evening. Cadman, President."

We are very grateful to Your Excellency for honouring us with your presence here to-night, and for consenting to propose the toast of the Institution.

At the dinner of the Institution, which was held in London last month, the same toast was proposed jointly by Sir Samuel Wilson and Sir Claud Hollis, and I am sure all present will agree with me that it would be difficult to find any more appropriate proposers than those who had administered the Government of, what is now, the largest oil-producing unit in the British Empire.

In some of the more sensational publications which purport to deal with oil, it seems to be the fashion nowadays to attribute all the ills of the world to the machinations of the oil companies, and the oil industry is made a scapegoat to cover a variety of political designs.

The aims of our Institution, which is closely allied with the oil industry, are mainly scientific, and we are very proud of the fact that the researches and discoveries of our members have contributed in no small measure to securing more economic development of the natural resources of the Colony.

At annual functions of this nature one is inclined to take stock of the developments of the past year and to speculate as to the future.

Our meetings during the year have been well attended, and the technical papers which have been read have maintained the high standard set in the past.

In the summer of this year I was glad to have the opportunity of attending a meeting in London between Members of Council of the Institution and those Chairmen and Secretaries of Branches who were at home at the time.

The meeting was arranged by Mr. Dalley, the Chairman of the Branch Committee, and, from the various proposals which were discussed, I can assure members that the Parent Institution continues to maintain a lively interest in the welfare of the Branches.

As regards the future, it would be a bold man who attempted to forecast the trend of world politics during the next twelve months, but in scientific matters we are on safer ground.

Membership of our Institution, and of kindred bodies, is not confined within the narrow bonds of nationalism, and research is not subject to the dictates of individuals.

Gradually the people of the British Empire have been learning the advantages of " thinking Imperially," and perhaps it is not too much to hope that, before it is too late, the peoples of the world will learn the advantages of " thinking internationally."

For the last five years it has been the privilege of the Chairman at these dinners to express the thanks of the Branch to our Hon. Secretary, Mr. H. W. Reid, for his numerous activities on our behalf during the past year. Reiteration does not mean that our thanks are any less sincere, and I would like to thank the members of the Branch Committee for all the assistance they have given me, and also those who have read papers and taken part in the discussions at our meetings. With such co-operation on the part of all concerned, the continued success of the Trinidad Branch is assured.

I should also like to take this opportunity, Sir, of wishing you and Lady Fletcher, on behalf of the members of our Branch, a very happy and prosperous term of office in the Colony.

## " The Industries of Trinidad."

The Toast of " The Industries of Trinidad " was proposed by **Mr. F. L. Melvill,** B.Sc., M.I.Chem.E. (Member), who said that the two major factors affecting the future of Trinidad industry were : firstly, the necessity for a continuance of the present sympathetic attitude of Government which had the effect of encouraging new capital, and secondly, a continuance of the excellent relationship between employer and employee.

In connection with the latter point, he felt that there was the necessity for a better appreciation by the Educational Authorities of the type of training best calculated to ensure the utilization by industry of the youth of Trinidad to their maximum benefit, and that the co-operation of the employers should be sought to ensure this. He did not refer to any form of specialized or technical training, but rather to the necessity for a more thorough grounding in what he termed general utility subjects, such as mathematics, science and English composition.

**Mr. A. Emlyn,** the President of the Chamber of Commerce, replied to the Toast.

"THE GUESTS."

**Mr. E. C. Scott,** M.C., B.Sc. (Associate Member), proposed the toast of "The Guests," to which **Colonel the Hon. A. S. Mavrogordato,** O.B.E., Inspector General of Constabulary, replied.

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## MR. G. SELL, LATE ASSOCIATE EDITOR

IT will now be common knowledge that the Associate Editor of the Journal, Mr. George Sell, has resigned his appointment. Mr. Sell has joined the editorial staff of *The Petroleum Times*, and all members will wish him the best of good fortune in his new venture.

Mr. Sell was concerned with petroleum in its earlier days. He was on Mr. Eastlake's staff and, of course, in that connection made frequent contacts with our first President, Sir Boverton Redwood.

He saw service in India and elsewhere during the War period.

He has been intimately associated with Institution activities for many years, chiefly as Associate Editor, but also as an admirable Secretary of the Standardisation Committee and as Librarian. He did excellent work as Co-Editor of the Proceedings of the First World Petroleum Congress. He was mainly responsible for the production of the Institution's Standard Methods for Testing Petroleum and its Products, and the Annual Reports on the Progress of Naphthology.

The Hon. Editor's tribute in the issue of *The Petroleum Times* for 2nd January may be quoted :—

> "Perhaps a few words from me concerning Mr. George Sell would be of interest to your readers. I speak more particularly of his activities in connection with the *Journal of the Institution of Petroleum Technologists*. Seeing that I have worked with him on that publication for more than 13 years, I am therefore well qualified to pay tribute to Mr. Sell's initiative, hard work, unvarying courtesy and utmost efficiency.
>
> "Anyone concerned with the publication of the *Journal* knows that not only must the staff be entirely *au fait* with all the technical services of make-up, printing, etc., but must have a good all-round knowledge of the innumerable subjects discussed therein. In both these directions Mr. Sell was admirable, and I can only say, personally, that his departure will be a great loss to the *Journal*, to the Honorary Editor and the Institution as a whole."

The Institution is greatly indebted to Mr. W. E. Gooday for his kindness in coming forward to fill the breach. Mr. Gooday is well known to members as a distinguished petroleum technologist, and with his co-operation it is believed that the *Journal* will still maintain its reputation as the foremost scientific publication on petroleum science.

A. E. D.

# THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE One Hundred and Seventy-fourth Meeting of the Institution was held at the House of the Royal Society of Arts, John Street, Adelphi, W.C., on Friday, January 8th, 1937, at 5.30 p.m.

LT.-COLONEL S. J. M. AULD, President-elect of the Institution, occupied the Chair at the beginning of the meeting. He said that it was a joint meeting of the Institution of Petroleum Technologists, the Institution of Automobile Engineers and the Royal Aeronautical Society, and expressed the opinion that such joint meetings were of the greatest value in giving an opportunity for the discussion of problems of interlocking interest in a way that was not possible at separate meetings of the various bodies concerned. He occupied the Chair as the representative of the President of the Institution of Petroleum Technologists, Sir John Cadman, who very much regretted his inability to be present. As the President-elect of the Institution, he was very gratified at the part taken by the Institution in the promotion of the present gathering. The Institution felt, however, that if full justice was to be done to the hearing and discussing of the paper that was to be read on the present occasion the meeting should be under the guidance of a gentleman who was known throughout the world as an authority on the internal-combustion engine, and it was with great pleasure that, on behalf of the three institutions concerned in the present meeting, he asked Mr. D. R. Pye, who was well known to most of those present as the Deputy Director of Scientific Research at the Air Ministry and a Member of Council of the Royal Aeronautical Society, to take the Chair.

LT.-COLONEL AULD then vacated the Chair, which was taken by MR. D. R. PYE.

THE CHAIRMAN (Mr. D. R. Pye) said that Mr. Wimperis, as President of the Royal Aeronautical Society, should be occupying the Chair rather than himself, but Mr. Wimperis was enjoying a few days' well-earned rest and had suggested that he should deputize for him.

Once upon a time internal-combustion engines were designed to accept anything which went by the name of petrol. Now they were much more particular, and the higher one went in specific power output the more particular they became, so that fuel and design in engines of the aviation class were intimately related—so intimately related that it could almost be said that a substantial improvement in the quality of the fuel available affected every detail of the engine. Therefore the designers of the aviation engine wanted to know what fuel would be available say, three years ahead,

because, when a man started to make a substantial alteration in the design of an aero engine, that engine was not likely to be in normal service for at least three years.

That emphasized the value of a paper such as that which Mr. Banks was to read on the present occasion. Mr. Banks was in a unique position for the giving of such a paper. He was so well known to members of the Royal Aeronautical Society that it was scarcely necessary to relate his history, but as there might be gentlemen present who had not come into contact with Mr. Banks, he would like to give some idea of the width of his engineering experience.

During the War Mr. Banks had been engaged in coastal motor-boats, and after the War he had been for four years with a firm dealing with the installation of marine Diesel engines. He had then become Experimental Engineer to the British Gnome and Le-Rhone Company, and then served for a time in the technical department of the Anglo-American Oil Company. Finally Mr. Banks joined the Ethyl Corporation as their technical representative in Europe, and it was by his work in connection with the use of tetraethyl-lead that he was best known. Mr. Banks was also primarily responsible for the development of the fuel used in the Schneider Trophy race and subsequently in the record-breaking Italian machine that achieved the world speed record. Mr. Banks' experience was unique both on the engine and fuel side, for his contacts extended not only over the whole of the United States, but throughout the length and breadth of Europe.

Those who had seen the proof of Mr. Banks' paper would realize the immense amount of matter that it contained. He had very wisely decided to cut it down to the shortest possible précis on the present occasion, so that sufficient time might be left for the discussion of it.

MR. F. R. BANKS then read a précis of the following paper :—

# SOME PROBLEMS OF MODERN HIGH-DUTY AERO ENGINES AND THEIR FUELS.

By F. R. Banks.*

## Introduction.

When I was invited to give this lecture it took me some little time to decide upon a subject which would be of sufficient interest to all those belonging to the three industries represented here to-night.

It is rather difficult nowadays to be original when at least half your audience knows quite as much, and probably more, than you do yourself, of some of the developments about which you are to speak. I have therefore endeavoured to give those who specialize in fuel some idea of the engine problems involved and, vice versa, the engine specialists some information on the latest fuel developments.

It is my experience that the specialist—and you are mostly specialists these days—often has little opportunity to get a general view of the whole scheme of things in which he is an important unit, and it is my hope this evening, therefore, to give you a view of the fuel situation and discuss some of the problems pertaining to present and future aero-engine development, as I see them; confirmed by my contacts with both engine manufacturers and aircraft operators.

Progress in aviation in Great Britain since the War has been mainly due to the aero-engine builder, and it is only comparatively recently that any real step forward has been taken in the design of aircraft.

Despite the fact that until a year or so ago little money was available, either for engines or air-frames, the engine-builders have shown a truly competitive spirit in always striving to produce a better product. By a better product I mean one which gives more power for a given cylinder capacity or swept volume, lower weight, lower specific fuel consumption and a more compact unit generally.

So far as the British manufacturer is concerned, there are two developments which have been mainly responsible for the big strides made in engine performance in recent years: first, the supercharger, and secondly and more recently, the great improvement in fuel quality. We led the world so far as supercharging was concerned, and I think we still do. The Americans taught us the importance of fuel quality and anti-knock value, and we are now speedily taking advantage of this knowledge.

As a result of these developments, power can be so increased that, coupled with the improvement which has also taken place in materials of construction, a specific dry weight of 1 lb. per b.h.p. is attainable on the basis of the take-off power rating of the engine.

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* Technical Representative, Ethyl Export Corporation, in Europe.

Whilst these two developments (supercharging and high anti-knock fuel) have been responsible for great improvements to date, I cannot see at the moment anything which will allow us to make such big jumps in future, unless it is a fuel which does not detonate or give rise to pre-ignition. Even then I doubt whether our technique is advanced enough yet to enable us to take full advantage of such a fuel.

Since engine design is an art and not a science (and will not be in our time), the future development of successful engines will be more a matter of detailed improvement, coupled with the use of improved materials of construction and still better fuels, than one involving any radical changes in design. That is not to say it will be a less expensive matter to develop engines in future; on the contrary, because it is not a science, engine development will always involve considerable experimental work and trial and error tactics. This will necessarily entail the scrapping of work which has taken many man-hours to evolve, before the desired end can be achieved.

This paper could not have been properly prepared without the assistance and advice of a number of individuals and firms, all of whom have given me much information, freely and unselfishly.

I desire to record my grateful thanks to the Ethyl Export Corporation for permission to present this paper and to Dr. Graham Edgar, Mr. S. D. Heron, Dr. G. Calingaert, Mr. K. Beaver, Dr. F. H. Garner, Mr. T. R. A. Bevan, Mr. H. Fossett, Miss B. Brown, Flt.-Lt. P. W. S. Bulman, Mr. J. R. Handforth, Mr. E. L. Bass, Mr. W. W. White and Mr. F. M. S. Tegner for their valuable assistance, advice and constructive criticisms.

Thanks are due to the Air Ministry for the kindly assistance and advice rendered by its various departments and in giving permission for me to have access to relevant tests and research reports, etc. In addition, the following firms and their technical staffs gave me valuable information and assistance: The AC-Sphinx Sparking Plug Co., Ltd.; Armstrong-Siddeley Motors, Ltd.; the B.G. Corporation; the Bristol Aeroplane Co., Ltd.; Champion Sparking Plug Co., Ltd.; the F.I.A.T. Co.; Thos. Firth & John Brown, Ltd.; Hawker Aircraft, Ltd.; Haynes Stellite Co.; High Duty Alloys, Ltd.; the International Nickel Co., Inc.; K.L.G. Sparking Plugs, Ltd.; D. Napier & Son, Ltd.; Pratt & Whitney Aircraft Co.; Rolls-Royce, Ltd.; the Scintilla Magneto Co., Inc.; Thompson Products, Inc.; Wilcox-Rich Corporation; Wright Aeronautical Corporation; Zenith Carburetter Co. Ltd.; K.L.M.; Mond Nickel Co.

Finally, acknowledgment is made to the Institute of Aeronautical Sciences, Inc., and to the Society of Automotive Engineers for the reproduction of papers comprising two Appendices.

## PART I.

### Present Fuel Position.

At the present time the greater proportion of high-duty engines in Great Britain, America and Europe, are developed to employ fuels of 87 octane number containing tetraethyl lead (leaded fuels); this rating being determined either by the C.F.R. Motor Method or the modified Motor

Method specified by the British Air Ministry. The latter test makes use of a mixture temperature of 260° F. instead of 300° F. in the former case. So far as leaded fuels are particularly concerned, there is a difference of approximately two octane numbers between the Motor Method and British Air Ministry tests; that is to say, a fuel of 87 octane by the latter test is equivalent to about 85 octane C.F.R. Motor Method.

The maximum amount of tetraethyl lead allowed in such fuels for commercial use is 3·6 ml. per Imperial gallon (3·0 ml. per U.S. gallon or 0·8 ml. per litre). For Governmental or military requirements this concentration may be doubled—that is, to approximately 7·0 ml. per Imperial gallon. In special circumstances the concentration may be increased to 4·5 ml. per Imperial gallon, for commercial fuels of 87 octane or higher.

The average amount of lead used in these fuels (of 87 octane) is generally in the region of 3·0 ml. per Imperial gallon, depending, of course, on the octane number and lead response of the basic spirit.

Recent developments in the U.S.A., on the part of the oil refiners, have enabled *iso*octane to be produced on a scale which allows it to be considered seriously as a constituent of aviation fuels. This material, as a chemically pure hydrocarbon (2 : 2 : 4-trimethylpentane), was originally found and developed by Graham Edgar [1] as a primary reference standard, and is used with normal heptane, for determining the knock-rating of fuels in terms of octane number.

Still more recent work has brought to light another blending agent, di*iso*propyl ether, which can be produced synthetically in adequate quantity.

It would seem that the production of aviation fuel is becoming more and more a matter of synthesis, with the oil companies operating as manufacturing chemists.

Before proceeding further, it might be helpful if some general explanation of the meaning of synthetic fuel were given.

The term " straight run " is applied to those gasolines refined by simple distillation, which merely separates from the crude oil the constituent hydrocarbons boiling in the desired gasoline range.

" Cracking " is essentially a high-temperature treatment which breaks up or " cracks " the heavier or larger hydrocarbon molecules, also rearranging their grouping. A fairly large proportion of the smaller molecules so formed are suitable for gasoline. The cracking operation involves a definite time, temperature and pressure treatment, which varies according to the type of cracking plant employed.

Until recently these two processes have been the only ones available for the production of gasoline, either for automobile or aircraft use. Within the last few years, however, processes have been developed for building up or synthesizing fuels, boiling in the gasoline range, from gaseous hydrocarbons. Such fuels may be conveniently classified as " synthetic fuels." Three developments along these lines appear worthy of discussion.

(a) *Polymerized Gasoline.*—Refinery gases formed in the cracking operation contain substantial quantities of hydrocarbons of the olefin class. By subjecting these to any one of the various combinations of temperature and pressure (with or without catalysts) chemical reactions occur which produce liquid fuel boiling in the gasoline range. Furthermore, the paraffinic compounds occurring in the refinery gases, or in natural gas or gasoline,

may be converted into olefins either as a separate process or simultaneously with the above process and converted similarly into gasoline.

Such fuel is known to the trade to-day as " polymerized " or " polymer " gasoline. Its chemical composition and other characteristics vary greatly with the particular conditions under which it is made. Aromatics, olefins, naphthenes and paraffins may be present, and the proportions of these constituents may vary greatly. The octane number is generally high (80–85 C.F.R. Motor Method), and the product appears to have real value as a blending agent with ordinary gasoline.

The high anti-knock value of polymer gasoline at once suggests it as an aviation fuel, but the available evidence does not, unfortunately, indicate that it will be very useful for this purpose. Most of the product now available is sensitive to operating conditions, and would appear to be of doubtful value in hot-running and high-duty engines. Also, its anti-knock value is increased relatively little by tetraethyl lead, which renders it of little use for the preparation of fuels of really high anti-knock value.

An interesting article by Egloff, on the catalytic treatment of cracked gases, has been published in *The Petroleum Times* (October 24th, 1936).

(b) iso*Octane*.—As mentioned previously, substantial quantities of commercial *iso*octane have recently become available, the raw material being the *iso*butylene obtained in somewhat small amounts from refinery gases. This is converted into di*iso*butylene by one of the several processes, and the latter on hydrogenation (either of the low or high pressure type) yields *iso*octane.

The boiling point of C.P. *iso*octane (2 : 2 : 4-trimethylpentane) is constant and is about 99·3° C. It is therefore unsuitable for use as a complete fuel in normal carburettor-type engines, and consequently, because of this, and since it is considerably more costly than ordinary gasoline, it is mostly employed as a blending agent with aviation gasoline; the fuel generally being completed to 100 octane number (U.S. Army Air Corps Method) by the addition of tetraethyl lead.

A typical 100 octane fuel of this type consists of a gasoline having an octane number of about 73 (C.F.R. Motor Method), with which is blended commercial *iso*octane in proportions varying between 40 and 50 per cent. by volume, depending on the octane number of the particular gasoline used and the limit set on lead concentration. The amount of tetraethyl lead added is generally in the region of 4·0 ml. per Imperial gallon.

In order to adjust the distillation range and to take care of different engine-induction systems, it is sometimes necessary to include a small proportion of volatile material such as *iso*pentane or stabilized casinghead gas.

The lead response of *iso*octane is very good, but as yet the present knock-testing methods do not show this up very well; in fact, some original work, in the United States, indicated that the addition of 3·6 ml. of lead per Imperial gallon to commercial *iso*octane was only equivalent to increasing its rating by about three numbers. But subsequent tests in a high-duty single cylinder showed that the addition of lead allowed the boost to be increased by about 14 per cent. above that for the pure material, giving a power increase of 17 per cent. Actually in this test the limit of *iso*octane plus lead was not reached due to limitations in supercharger capacity.

A paper by Klein,[2] describing the original work done by the U.S. Army Air Corps on *iso*octane, together with a letter written subsequently, is reproduced in the form of an Appendix to this paper (Appendix I).

(c) iso*Propyl Ether.*—*iso*Propyl ether, or, to be more correct, di*iso*propyl ether, is the most recent development in the synthesis of fuels on a production basis. It is an excellent anti-knock material, having a good lead response, and its potentialities from the production aspect appear to be far greater than those of *iso*octane.

*iso*Propyl ether was first found for this purpose by Buc, who, with Aldrin, presented a paper describing its features and uses.[3]

The raw material from which *iso*propyl ether is produced is propylene, present in refinery gases (or made by cracking propane from natural gas), this (propylene) under appropriate chemical treatment reacts to form *iso*-propyl ether.

*iso*Propyl ether is what is known as a branched-chain ether, and its physical characteristics, compared with those of *iso*octane and benzene, are shown in Table I, which is reproduced from the paper previously referred to.

TABLE I.[3]

*Physical Characteristics of Pure Compounds.*

| | *iso*Propyl Ether. | Pure *iso*Octane. | Benzene. |
|---|---|---|---|
| Boiling Point, ° F. at 760 mm. Hg. Pressure | 154 (153–158) | 211 | 175 |
| Density at 68° F. (20° C./4° C.) | 0·725 | 0·691 | 0·878 |
| Refractive Index at 68° F. | 1·3680 | 1·3921 | 1·5014 |
| Freezing Point, ° F. | — 125 * | — 162 | 42 |
| Viscosity, Centipoise | 0·322 (68° F.) | 0·543 (65° F.) | 0·647 (68° F.) |
| Latent Heat of Vaporization, B.Th.U./lb. | 123 | 130 | 170 |
| High Value of Heat of Combustion, B.Th.U./lb. | 16,900 | 20,580 | 17,650 |
| Low Value of Heat of Combustion, B.Th.U./lb. | 15,600 | 19,200 | 17,000 |
| Low Value of Heat of Combustion plus Latent Heat of Vaporization, B.Th.U./gallon | 95,100 | 111,400 | 125,700 |
| Reid Vapour Pressure, lbs./sq. in. at 100° F.† | 5·3 | 2·2 | 3·2 |

* Particular emphasis should be placed on the freezing point of *iso*propyl ether. Freezing which has occurred with benzole in practice may have been due to benzole itself. Some freezing has occurred at very high altitudes and low temperatures in exposed fuel systems from water obtained in ordinary gasoline. Also, attention is directed to the latent heat of vaporization for *iso*propyl ether, it being even better than gasoline from the carburettor–refrigeration standpoint.

† Reid Vapour Pressure determined on commercial products rather than C.P. compounds. In case of benzene, vapour pressure value is for commercial 90 per cent. benzole.

According to Buc and Aldrin, *iso*propyl ether, when blended in ordinary aviation gasolines, will produce a fuel of 100 octane (U.S. Army Air Corps test) with a lead concentration not exceeding 3 ml. per U.S. gallon (3·6 ml. per Imperial gallon).

Heron [4] has reported the octane number of *iso*propyl ether as 98·5 (U.S. Army Air Corps test method), and from the evidence available (Buc and Aldrin) it appears to have a slightly superior blending value to that of commercial *iso*octane, and is also superior for a given lead concentration in the corresponding blends.

The lead concentration in *iso*propyl ether, in order to obtain a given octane number, is lower than that necessary for technical *iso*octane for the same knock rating.

*iso*Propyl ether has one important disadvantage, which is its lower calorific value relative to that of *iso*octane. The difference is in the order of 19–20 per cent., but when considering comparative blends of 100 octane fuel, in one case employing commercial *iso*octane, and in the other *iso*propyl ether, this difference is reduced to about 7 per cent.; which, however, is still somewhat on the debit side, and is a serious disadvantage from the point of view of fuel economy.

Since the question of fuel economy is becoming more and more important, it may be difficult to convince those concerned with aircraft operation that *iso*propyl ether has any advantage over *iso*octane, but it must be remembered that the former will probably be more readily available than the latter, particularly in European countries or in those places where there is little or no oil production and refining or cracking facilities.

Again, since *iso*propyl ether will probably be much less costly than commercial *iso*octane, and although the question of fuel economy is very important, the latter is not necessarily a primary consideration for military fighters or commercial aircraft, for flights of short duration.

*iso*Propyl ether is not, however, intended to displace *iso*octane, but to be complementary or supplementary to it, as a blending agent for fuels of high anti-knock value. It may be used with *iso*octane, and data are available (Buc and Aldrin) to show that a 50-50 blend of the two in standard knock reference fuel C-9 has a superior anti-knock value to *iso*octane alone, in the same reference fuel.

The availability of *iso*octane may be so limited in some countries, and the cost so high, that it will not be considered either from a military or commercial standpoint, and in this case *iso*propyl ether might be preferred. If this were so, its lower calorific value would be of no great disadvantage, because when employed for an 100 octane fuel it would then probably be compared with one of 87 octane, in which case engines could be developed to show decided advantage with the former fuel over the latter, despite the former's lower heat value.

*The Alcohols.*—I feel that the alcohols have not justified themselves as constituents of aviation fuel, even in those countries where the respective Governments have fully supported their use by subsidy or monopoly. Although there are many objections to the employment of the lower alcohols in aviation fuel, the following information may be of some interest.

The alcohols generally used are ethyl ($C_2H_5OH$) and methyl ($CH_3OH$), both of which can be produced by synthesis (known then as ethanol and methanol).

Ethyl alcohol, the one generally employed, is usually blended with gasoline; but because of its relatively low calorific value (some 40 per cent. less than gasoline) and high specific gravity, the fuel consumption is

somewhat increased (according to the percentage added) and a greater weight of fuel must be carried. Methyl alcohol has yet a lower calorific value than ethyl, by about 22 per cent.

Further, these lower or water-soluble alcohols are difficult to blend with gasoline unless they are substantially anhydrous, and their storage is somewhat of a problem, since either the presence of small percentages of water or a reduction in temperature brings about separation.

Alcohol blends can also cause considerable corrosion and solvent troubles with the materials which are generally used in the construction of aviation engines and their components, such as the aluminium alloys used for fuel tanks, carburettor float-bowl castings, supercharger casings, induction manifolds, also the fuel-system jointings, etc.

The principal advantage of the alcohols, ethyl and methyl, is that they each have a high latent heat of vaporization relative to that of gasoline. Even when blended with gasoline, in amounts up to about 20 per cent. of alcohol by volume, this feature is particularly valuable in reducing the "boost," or supercharge, temperature; thus allowing a greater charge weight to enter the cylinders of the engine, and thereby improving its power output.

The anti-knock value of these two alcohols is high, and it is a feature that they do not detonate in the ordinary sense of the word, but they can, and do, pre-ignite violently when subjected to certain operating conditions in the engine. I know of two or three authentic cases, where fuels consisting of about 20 per cent. of ethyl alcohol, by volume, in gasoline, plus lead, gave rise to very rough running and pre-ignition, whereas the same engines would operate quite satisfactorily with a leaded gasoline of equivalent octane number.

An actual case was one in which the engine concerned gave a specific fuel consumption of about 240 grams (0·530 lb.) per b.h.p.hr., with a leaded gasoline and at its full rated power; after which a blend of 20 per cent. ethyl alcohol in gasoline, plus lead, was tried, and the mixture strength adjusted to allow for the fall in calorific value due to inclusion of the alcohol. This gave a specific fuel consumption of 260 grams (0·580 lb.) per b.h.p.hr., but at that figure the operation was so rough and erratic the consumption had to be increased to 290 grams (0·645 lb.) per b.h.p.hr., and even at this high figure it was not possible to obtain the same power from the engine as it gave with the "straight-run" leaded gasoline. The engine in question was a large "two-valve" air-cooled radial.

Another engine of the same type, but of more modern design and higher power, would not run on a fuel containing 30 per cent. of alcohol without severe pre-ignition, even although a large concentration of lead was used. In the case of this latter engine the sparking-plug shell temperature reached the high figure of 300° C. However, it operated quite satisfactorily on a leaded gasoline, without alcohol. Both engines were fitted with sodium-filled exhaust valves.

Similar alcohol fuels have given quite satisfactory running in liquid-cooled engines with jacket temperatures, varying in individual types between 80° C. and 125° C. These engines were of the "four-valve" flat combustion-head variety, having smaller cylinders than the air-cooled radial types cited in the foregoing tests.

I am, however, aware of a well-known 9-cylinder air-cooled radial engine with a cylinder design incorporating four valves in a pent-house type of combustion chamber; this particular engine has given satisfactory operation with alcohol blends similar to those used in the tests just described. No pre-ignition has been experienced under similar conditions of operation. This engine is also fitted with sodium-filled exhaust valves.

Therefore, although it would be unsafe to dogmatize regarding the use of these alcohols as constituents of aviation fuel, they appear to be very critical to operating conditions, and their employment is uneconomical.

The higher alcohols, such as *iso*propyl, have been investigated, but do not, at the moment, appear to offer any particular advantages.

## Fuel Rating and Correlation.

One of the principal difficulties in the rating of fuels is that of correlating the laboratory knock-test results with the performance of the same fuels in full-scale engines. Since there are a large number of engine types to satisfy, and it is scarcely practicable to have a different laboratory test method for each type, one can only hope for one which will give good average results.

There are three knock-testing methods in use to-day for rating fuels; these are: the C.F.R. Motor Method, the C.F.R. modified Motor Method specified by the British Air Ministry, and the U.S. Army Air Corps test. As previously explained, the only difference between the first two tests is that of the mixture temperature; the C.F.R. Motor Method is too well known to necessitate taking up time and space in describing it.

The U.S. Army Air Corps test varies considerably from the "Motor Method," and employs a modified C.F.R. unit which has a smaller cylinder than the standard engine ($2\frac{5}{8}$ inch bore instead of $3\frac{1}{4}$ inch).

The bouncing pin is replaced by a temperature plug communicating direct with the combustion chamber.

The engine runs at 1200 r.p.m., and is fitted with a special 5-ring aluminium piston, a stellited exhaust valve having a sodium-filled stem, and an unshrouded intake valve. High-temperature cooling is employed, the jacket temperature being 165° C. A standard C.F.R. down-draught carburettor is used with the exception of the mixture heater; "cold" induction being employed for this method.

The standard knock intensity or temperature plug reading, for each particular engine or cylinder and piston combination and temperature plug, is determined by adjusting the mixture strength to give the maximum plug reading for C.P. benzene, and also that for a blend of 88 octane and 12 heptane. When these two settings have been obtained, the compression ratio is adjusted to give the same temperature plug reading on both fuels. In addition, a check is made to see that no pre-ignition is present, by cutting the ignition switch when the engine is running under these conditions.

The degree of knock is assessed by means of temperature plug readings on a potentiometer, and for each fuel under test the mixture strength is that which produces a maximum reading of the temperature plug for the specified engine conditions.

Briefly, the procedure for matching a fuel is to check a sample of it

against the required primary or secondary reference standard, with the engine adjusted as previously described, to see if it meets the desired anti-knock value. The temperature plug reading, for a match, should then be the same as that for the reference standard.

If desiring to ascertain the anti-knock value of a sample, the engine is adjusted to standard knock intensity, or set to avoid pre-ignition and checked by cutting the ignition switch, as previously described, and the anti-knock value of the sample is found by making a blend of the primary or secondary reference standards to match it.

According to the present methods of fuel-knock testing, and referring to those tests which I mentioned in the section dealing with *iso*octane; Edgar [2] has pointed out that an octane number, as a unit, possibly increases in value, or becomes more effective, in the higher range, between 90 and 100, than in the lower range, say between 70 and 80 octane.

In other words, a difference of two octane numbers in the 90–100 octane range will mean much more to an engine, taking full advantage of the fuel, than a similar difference in the 70–80 octane range.

Although the three knock-testing methods discussed are not entirely satisfactory, as our technique improves and our knowledge of fuels increases better methods will be evolved which will tend to rate fuels more accurately and give superior correlation.

The Army method appears to give superior reproducibility as compared with the C.F.R. Motor Method test, and is apparently less liable to give variable results in the higher octane number range. It is not, however, so sensitive as one would wish in rating fuels in the 100 octane class, particularly for determining accurately the effect of tetraethyl lead concentrations in such fuels.

Table II gives the results of tests (" Army Method "), by three different laboratories in the States, on three different samples of fuel, all of approximately 100 octane number. The results indicate the high degree of reproducibility which it is possible to obtain by this method.

Table II.

| Laboratory. | Sample Nos. | | |
|---|---|---|---|
| | 1. | 2. | 3. |
| 1 | 100 | 98 | 97 |
| 2 | 100 | 99 | 98 |
| 3 | 100 + 0·1 ml. of lead per U.S. gallon. | 100 | 98·5 |

The principal reason why the C.F.R. Motor Method is unsuitable for rating 100 octane fuel is that the compression ratio can be raised so much with this fuel, that the resulting combustion pressures operate the bouncing-pin before detonation occurs; consequently, it is necessary to depart from the standard test procedure accepted (tentatively) by the American Society for Testing Materials (A.S.T.M.), and employ a non-standard and arbitrary one which involves the use of a large bouncing-pin gap, etc.

This necessary departure from the standard cannot render more accurate

the method of rating 100 octane fuel, because although it is usually matched against a primary reference standard of C.P. *iso*octane 2 : 2 : 4-trimethyl-pentane, there is no definite procedure to work to, and the somewhat coarse bouncing-pin setting gives knock-meter readings which must depend on the operator of the unit still more for a reasonable interpretation of the relative knock intensity of the sample, and also the primary reference standard. This does not make for a high degree of accuracy or reproducibility from engine to engine, or between different laboratories.

Some work has been done by the Shell Company at their Delft Laboratory, where they have supercharged a C.F.R. engine in order to investigate the possibilities of improving the rating methods for fuels and obtain better correlation with full-scale engines. This work has not yet progressed far enough to enable any conclusions to be reached, but an article published in *Aircraft Engineering* [5] gives some idea of the ground covered.

Whilst the Army method may be superior to the C.F.R. Motor Method for rating fuels above 87 octane, the latter is fairly satisfactory for those up to 87 octane, and will give reasonably good correlation with full-scale engines if the fuels concerned are of the " straight-run " and/or leaded variety and contain only a small percentage of aromatics.

It is interesting to compare the ratings obtained on the same fuels by the different knock-test methods; for instance, the " Fighting Grade " fuel in general use by the U.S. Army Air Corps to-day (Air Corps specification No. Y-3557-G) is nominally rated at 92 octane by the Army method (Air Corps specification No. 3566), and is equivalent to 87 octane, C.F.R. Motor Method. This is usually a straight-run leaded fuel. Benzole is rated by the C.F.R. Motor Method in excess of 100 octane, but by the Army method is only given a value of 88 octane.

It will be deduced from the foregoing that the Army method depreciates aromatics, and it was designed to do this when it was evolved, because fuels containing a fairly high proportion of aromatics, and also those fuels containing cracked stock, were then similarly depreciated in American full-scale engines.

Since that time, and due to improvements in the cooling of cylinder heads, etc., such fuels are not now depreciated to the same extent; and indeed there is evidence that improvements in design have so reduced the " hot spots " in the combustion chamber that the aromatic fuels are now mostly appreciated relative to the Army method and the C.F.R. Motor Method, despite the fact that the specific duty of the aero engine has also increased. In some cases the degree of appreciation is equivalent to as much as 7 or 8 octane numbers, C.F.R. Motor Method.

The modified " Motor Method " test, used to rate fuels meeting the British Air Ministry specifications, D.T.D. 224 and 230, is less severe on them than the " Motor Method." But it also tends to de-rate the aromatics relative to full-scale conditions; at least so far as British engines are concerned, and particularly the liquid-cooled types.[11]

Whilst the aromatics showed to advantage, in these tests, at normal and rich mixture strengths; upon leaning the mixture this advantage was not apparent.

Fuel meeting the " 224 " specification does not contain tetraethyl lead, but may include aromatics in certain proportions; such fuel has been shown

to appreciate in full-scale liquid-cooled engines, by the equivalent of 8 or 10 octane numbers in some cases.

An octane number is not, therefore, an absolute value, and I have shown that it can, in fact, differ considerably in effective anti-knock value, according to the type of fuel, the particular laboratory knock-test method employed, and the conditions to which it is subjected in full-scale engines. But we are now aware of these facts, and can, from the experience gained as the result of laboratory tests and practical work with full-scale engines, rate fuels so that a reasonably satisfactory estimate of their relative values can be obtained. The rating of fuels was most uncertain until two or three years ago, and prior to that period engines were liable to suffer accordingly; even now a slip up in laboratory technique sometimes occurs and causes considerable trouble.

So far, I have not said much about the actual procedure of obtaining correlation between the knock-testing unit and the full-scale engine; and whether a single cylinder of the latter can be used to check a set of knock-testing conditions which will rate fuels in their order of merit, and give correlation with the multi-cylinder engine. Obviously, to employ a single cylinder of the full-scale engine is desirable, if only on the score of cost and simplicity, because full-scale tests are exceedingly expensive, and take considerable time.

An investigation has been made in America, employing full-scale engines, in order to find whether or not the C.F.R. " Motor Method " is a satisfactory test for rating fuels. The method was confirmed as suitable for fuels having octane numbers up to and including 87.

This investigation, the results of which have been reported in a comprehensive paper by Veal,[6] was very ambitious, and it confirmed, also, the variations that can occur, between the laboratory unit and full-scale engines, with the aromatics. In one case the " spread " was as much as 7–8 octane numbers. But it was apparently thought that these variations should not influence the recommendation for the adoption of the " Motor Method."

The investigation did not prove, however, that similar work could not be done almost as satisfactorily on single-cylinder units of full-scale engines, nor was it intended to. But I am now of the opinion that single cylinders could be used under carefully controlled conditions; particularly since the distribution of fuel in the multi-cylinder engine has so improved that the differences between individual cylinders are now small. Which means that, in the case of making a consumption " loop "—that is, plotting b.m.e.p. against fuel consumption or fuel flow—similar characteristics and effects should be capable of reproduction both in the multi- and single.

Naturally, the final answer has always to be provided by the full-scale engine, and, whatever method of rating is adopted, fuels will be given their real test by this means. In endeavouring to obtain correlation and a satisfactory knock-testing method by means of a single-cylinder unit, a great deal of ground can be covered quickly, and a number of fuels tried, and perhaps eliminated, before submitting the final selection to a full-scale test.

The operating conditions for the single-cylinder unit could consist of running consumption " loops " on each fuel sample, at a constant engine speed similar to that of the full-scale engine, and at a given knock intensity controlled by the boost pressure.

Knock intensity is naturally the most difficult condition to satisfy, and I have no original suggestions to make regarding its measurement. But I suggest that a thermo-couple embedded in a temperature-sensitive part of the combustion chamber, or in the nose of the central electrode of the sparking-plug, might be satisfactory.

Personally, I favour a serious trial of couples in the sparking plugs, and I think that such a test would be well worth while. The plugs would have to be kept clean for each test, and the only other difficulty might be that of the thermal contact offered by the thread, which may vary somewhat from plug to plug, due to differences in thread form.

To detect and assess detonation aurally is not, in my opinion, good enough, because although some operators become very skilled in employing this method, the human ear is not sufficiently sensitive to pick up the immediate onset of detonation. This applies particularly in the case of the so-called non-knocking fuels such as benzole, ethyl and methyl alcohol, which do not detonate in the ordinary sense, but are often characterized by a marked temperature rise which is noted at the walls of the combustion chamber, and if allowed to continue will probably lead to violent pre-ignition. Detonation can occur when they are blended with gasoline, but the knock will be different from that of a straight-run gasoline, with or without lead, or one containing a high percentage of *iso*octane, such as an 100 octane fuel.

I am hoping that some satisfactory method of indicating the pressures in the cylinder, or cylinders, of a high-duty high-speed engine will soon be found. Perhaps the cathode-ray indicator will be developed to do this, and enable us to determine accurately the onset and degree of detonation.

So much for the various problems relating to the production of modern fuels and the difficulties of rating and correlation. I now propose to confine myself to engine development so far as it concerns the employment of fuels containing tetraethyl lead, and particularly those of 87 octane (C.F.R. Motor Method) and 100 octane number (U.S. Army Air Corps method), because these two fuels are now accepted and are in use to-day.

The former—87 octane—is in general use throughout the world, and the latter is being more and more employed by the U.S. Army Air Corps and the U.S. Navy. The aircraft-operating companies in America, in conjunction with the engine manufacturers, are investigating the possibilities of using 100 octane fuel in order to obtain lower fuel consumption and increased range or pay load.

The British Air Ministry is shortly issuing a provisional specification for 100 octane fuel. The object is to obtain data and experience regarding its use, and also to allow the engine-builders to set up a standard on which they can base future developments.

## PART II.

### Engine Development.

The rapid progress in engine development has only been made possible by the enthusiasm of the design and experimental staffs of the engine builders, and their close co-operation with outside concerns such as the suppliers of material and the fuel and oil companies; and in this country the Air Ministry, which is their biggest customer.

In the last year or so the pace has been so rapid that troubles, which had been overcome in the early stages, have re-occurred later due to the big increase in engine performance.

Instances of this can be quoted; such as exhaust valve burning, which was generally cured in most engines, but, because of a large increase in duty, returned in some. Similar cases can be cited for valve-spring breakages, bearing and also sparking-plug failures; until it seems that we will never be free from some major trouble for long.

However, this is the price we must always pay for progress, and things will not be very different in this respect in a hundred years' time; but without difficulties to surmount nothing can be learned.

## Cylinder Head and Combustion Chamber Design.

I do not think that "fancy" combustion-chamber shapes are necessarily desirable for high-duty supercharged aero engines. That is to say, those shapes specifically designed to promote turbulence, improve combustion, and avoid detonation.

The principal considerations which should determine the design of a cylinder head and combustion chamber are as follows:—

(*a*) The provision of good breathing facilities; that is, adequate valving.

(*b*) Efficient means of cooling the valves, by sodium and good seat, guide and port design.

(*c*) A design of cylinder head in which the most satisfactory sparking-plug positions can be determined, by single-cylinder tests if necessary, so that they will be very well cooled in whatever position is finally decided for them.

(*d*) In the particular case of the cylinder head of a liquid-cooled engine, the passages for the liquid should be designed so that they have a good chance of being made according to drawing, by the foundry or shop.

Some will consider that these remarks are rather obvious, but too much stress cannot be laid on the need for adequate cooling of the combustion chamber as a whole. And this particularly includes the valves and sparking plugs.

A superior performance and lower fuel consumption will be possible, with a fuel of given octane number, if very careful attention is paid to these matters, to say nothing of the increased life of exhaust valves and sparking-plugs.

The difficulties attending the efficient directing of the cooling medium for liquid- and air-cooled cylinders are reversed in some respects. In the case of the liquid-cooled cylinder, it is a comparatively simple matter to collect the liquid and push it through the jackets. But due to the fact that modern engines of this type generally have cast aluminium alloy heads and jackets, the difficulties inherent in this design, and the limitations of foundry work, often prevent the passages from being produced as originally designed. Consequently, the liquid may not be directed properly to those parts requiring it, and overheating, severe stressing and distortion will occur in the cylinder block.

Unlike the former type, the air-cooled cylinder can be made almost

exactly as designed, but in this case the cooling medium is more difficult to collect and direct.

It might be preferable if the liquid-cooled cylinder reverted to its original form—that is to say, returned to the welded steel-jacket construction. At least one would be sure that the coolant space could be reproduced as designed, and by applying modern practice a very successful engine might be developed along these lines.

The fabricated steel cylinder head, of the type originated in German engines, might not be at all unsatisfactory as a performer; and the design employed for the Rolls-Royce "Condor" engine gave very good results as regards power.

The only arguments which can be advanced against the use of this type of construction are: that, when employed in the form of separate cylinders, it does not contribute to the rigidity of the crankcase and engine as a whole, and, also, the pitch of the cylinders is generally increased relative to that which can be used in block construction. This makes for a longer crankshaft and unit generally, for a given cylinder size.

Actually, there is no reason nowadays why such cylinders cannot be built up in block form or tied together by some means. In any case, so far as crankcase rigidity is particularly concerned, it is possible that in a few years' time, when the performance is still further increased, forged or stamped, and built up crankcases will be necessary for liquid-cooled engines.

The types of combustion chamber which, for the want of a better word, I have termed "fancy," have mainly been developed for automobile engines, particularly those of the side-valve variety. In this sphere they have mostly been quite satisfactory in reducing the chances of detonation, especially since only one sparking-plug per cylinder is usually fitted; for reasons of price and simplicity.

The automobile engine is normally unsupercharged, and probably does not have the induced turbulence of the supercharged aero engine. Whether or not this is of great consequence is a matter for conjecture, but the main argument against such combustion-chamber designs for the aero engine is that the differences in section, which are practically unavoidable with cast material and odd shapes, create masses which would probably act as heat accumulators in the case of the aero-engine cylinder. Particularly since it has to deal with considerably more heat per minute than the normal automobile cylinder.

I do not mean that it is not worth while to experiment with the cylinder head in other ways; such as by trying out streamline and/or venturi valve ports, and inlet ports arranged so that the mixture enters the cylinder tangentially, etc. All such work is well worth doing, and may further improve a well-designed symmetrical head.

In Fig. 1 are shown three different combustion chamber shapes and four different valve arrangements which are in use to-day on various aero engines.

1. This is the four-valve pent-house so successfully developed by the Bristol Company, which allows very good breathing at comparatively high piston speeds, due to the large valve area and the relatively small mass per valve. The latter feature ensures freedom from valve bounce and other mechanical difficulties attending high-speed operation.

The arrangement is probably one of the best compromises when all the requirements for a modern engine are considered, particularly so far as high-speed operation is concerned.

2. The two-valve hemispherical head shown here represents common practice in America, and is employed for practically every air-cooled engine manufactured in the United States. It gives a symmetrical combustion chamber which is easy to machine, and it also provides a very clean entry and good fin exposure and arrangement, for air cooling.

Since the cylinder heads of all the representative air-cooled radial engines in the United States are in cast aluminium alloy, the two-valve head of this form allows for simple and relatively low cost production.

The objection to this arrangement—and a major one, in my opinion—is that for large cylinders of about 6-inch bore, it involves the use of big valves, in the order of 3 inches diameter; and the hollow head, sodium cooled,

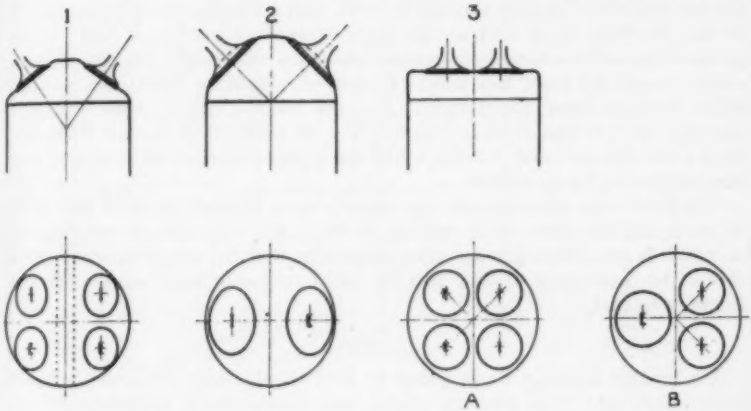


FIG. 1.

exhaust valve for such a cylinder weighs about a pound. This means that the operational speed must be restricted because of the considerable valve mass involved. Consequently, most of the high-duty American engines normally run at lower speeds than similar British engines, and therefore at a generally higher b.m.e.p. for a given total output.

3. Here are shown two valve arrangements for the flat-type combustion chamber generally employed for liquid-cooled engines.

In its original form, the cylinder was of the closed-end type, having a steel head integral with the barrel; this was not in direct contact with the cooling liquid, but depended on the thermal contact between it and a cast aluminium alloy header containing the coolant, and incorporating the valve porting and operating gear.

This should not be confused with the earlier type of cylinder, mentioned previously, with a sheet jacket, which allowed the liquid to be in intimate contact with the outer surface of the combustion chamber.

Because of inferior heat transfer and dissipation, the closed-end cylinder

has been discarded for an open steel barrel and a cast aluminium alloy combustion chamber and head carrying all porting and valve gear.

The flat head fits in very well with the typical liquid-cooled engine having block cylinder construction, and it allows a compact cylinder head and simple valve-operating mechanism to be used; both of which are more difficult to arrange in the case of pent-house or hemispherical heads, having valves set at fairly wide angles.

It is practically necessary to have three or four valves in this head, because of the limited head area available for adequate porting. With two valves only, the engine would be somewhat throttled.

One would advise such a head-and-valve arrangement for a comparatively high-speed engine having a large bore to stroke ratio. This latter feature would enable ample valve area to be provided, and allow three or four valves of small individual mass to be operated fairly simply.

It is interesting to recall that the racing Napier "Lion" engine, built for the Schneider Trophy Contest in 1927, had a closed-end cylinder barrel of the flat-head type, and a very high compression ratio of 10/1. This gave a thin, or biscuit, section combustion space, that might not be regarded very favourably from the point of view of obtaining good combustion, with freedom from detonation. But the engine, which was unsupercharged, gave a specific fuel consumption of about 0·32 lb. per b.h.p.hr., with a suitable fuel, and, I believe, had the highest thermal efficiency of any heat engine so far produced.

The four-valve arrangement has usually been that adopted for this type of head, but the three-valve version shown in 3(*b*) has much to recommend it, and it is not difficult to see, by comparison, that the single exhaust valve should be more easy to cool and the head probably more simple for the foundry to cast.

## Valves.

Under this heading I am going to deal particularly with the exhaust valve problem. The modern engine has made heavy demands on the exhaust valve, and supercharging, particularly, has been responsible for a considerable increase in its working temperature.

Engines such as the "Pegasus" and the latest Wright "Cyclone" now give over 100 b.h.p. per cylinder for take-off power, which means in the latter case more than 100 b.h.p. per exhaust valve.

Since high-duty fuels (87 and 100 octane) all contain tetraethyl lead, the exhaust valve must be developed to resist hot corrosion attack. But with modern technique this is not now a major problem, and it is possible to obtain satisfactory operation over long periods without suffering valve burning.

There is now adequate evidence to indicate that hot corrosion attack of the valve steel is largely due to the action of a small amount of free lead oxide, at high temperature, which has not been entirely eliminated by the ethylene dibromide. The latter is included in ethyl fluid in order to convert the lead oxide, formed during the combustion process, to lead bromide; which is then expelled through the exhaust ports in volatile form.

The Rolls-Royce laboratory has recently investigated the action of lead oxide at high temperature on materials such as Stellite; and re-

produced in Fig. 2 is a curve showing the rate of hot corrosion attack by lead oxide on samples of Stellite, kept at various temperatures for four hours. This is in the nature of a preliminary investigation, and Messrs. Rolls-Royce, Limited, have kindly allowed me to reproduce the curve prepared by their laboratory. It will be noted that there is a comparatively safe range up to about 650° C., after which the rate of attack increases

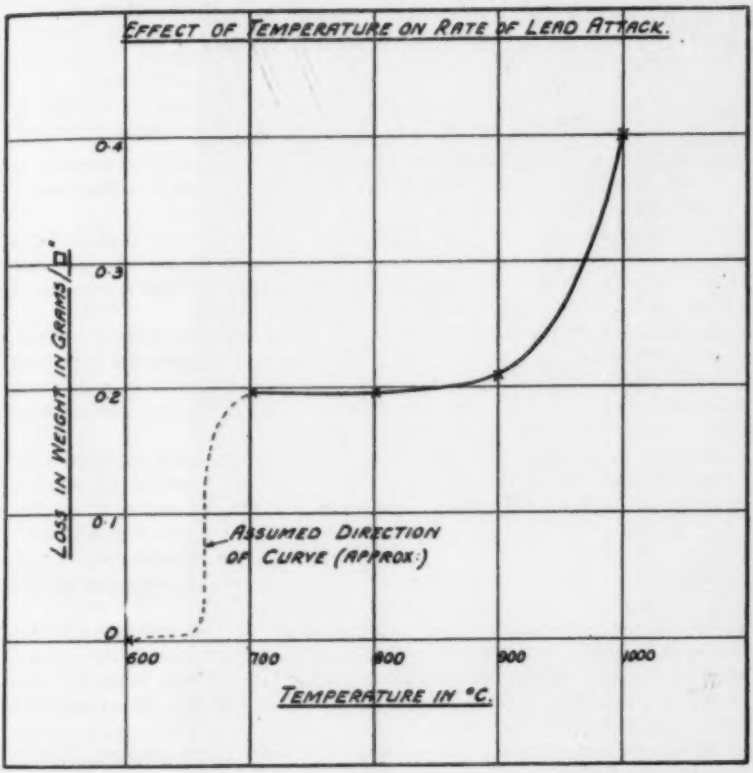


FIG. 2.

rapidly until it reaches 700° C., at which it remains more or less constant until 900° C., when another very rapid increase again occurs.

A simple method of determining whether or not the valve steel has suffered hot corrosion attack is by means of an ordinary pocket magnet. Austenitic steel is non-magnetic, but the scale from this attack will consist of magnetic iron oxide, and this can be checked very easily by the magnet.

There are two methods of combating valve burning: first, by cooling the valve adequately, usually with sodium filling in the stem and also the head; secondly, by the use of valve steels having a high resistance to corrosion. Naturally, these methods are used in combination in order to

make a satisfactory valve which will be corrosion-resistant under all working conditions.

The most popular valve material in use to-day is an austenitic steel to the general composition given in Table III.

TABLE III.

| | |
|---|---|
| C | 0·35– 0·45 per cent. |
| Cr | 12·50–14·50 „ „ |
| Ni | 12·50–14·50 „ „ |
| Mn | 0·50– 1·00 „ „ |
| Si | 1·00– 1·75 „ „ |
| W | 2·00– 3·00 „ „ |
| S | not more than 0·03 per cent. |
| P | „ „ „ 0·03 „ „ |

This steel has proved most satisfactory; it has a high resistance to hot corrosion attack, and does not suffer from cold corrosion in the form of rusting of the valve stem.

Practically every exhaust valve now used in modern aero engines has a stellited seat; since Stellite has a much greater resistance to corrosion attack than the present valve steels, it is absolutely necessary to use it to obtain satisfactory valve life and freedom from burning.

American engines generally employ the hollow-head variety of sodium-filled valve, and, coupled with good guide cooling, to remove the heat from the valve stem, it usually runs very cool indeed; particularly considering the high operating duty. Its temperature is probably not greater than 650° C. under full load conditions.

Present British practice is to use a valve having a sodium-filled stem only. Because of this the valve-head is apt to run somewhat hotter than that of the hollow-head type, consequently a greater degree of scaling and corrosion of the head surface, exposed to the combustion chamber, occurs. If this scaling is allowed to persist, it sometimes causes pre-ignition under high duty conditions. To avoid scaling, the practice has been to Stellite the whole surface of the valve-head.

Whilst Stellite, applied to the valve seat, has a high resistance to corrosion and erosion, it has been found, when using it for treating the exposed side of the valve-head, that it is practically completely removed after about 50 or 100 hours of high-duty running; leaving an exceedingly rough and irregular head surface.

At first, it was thought to be due to the technique employed in depositing the Stellite on the head, but this does not appear to be the case. Possibly, since it has mainly been used for stem-cooled valves, where the head runs at relatively high temperature, the heating and cooling, and also the flexing of the head, causes cracking of the thin Stellite layer, giving rise to corrosion or erosion at the cracks.

Another material has been found for this purpose which seems to be quite satisfactory, and does not appear to suffer from the same defect. This is known by the trade name of "Brightray," and is produced by Messrs. Henry Wiggin & Company, Limited.

"Brightray" consists of about 80 per cent. nickel and 20 per cent. chromium, and it appears to require a somewhat higher temperature of application, relative to Stellite.

Since austenitic valve steels are inclined to cause "pick-up" in the

valve guide, and also because of their relatively high coefficient of expansion, it was the practice to give rather large guide clearance. But now that cooling, by means of sodium, is possible, it is more necessary to see that the whole valve port and guide arrangement is designed so as to dissipate the heat from the stem efficiently. Consequently, the valve stem is often nitrided to avoid "pick-up" between it and the guide material, and as small a guide clearance as possible is then given, in order to obtain good thermal contact. I believe that the guide clearance in the case of the "Cyclone" exhaust valve is 0·004 inch for an $\frac{11}{16}$-inch diameter stem.

To obtain good seating under all conditions it has been British practice to use a valve which runs with a fairly hot head, so that it conforms better to any distortion of the inserted seating in the cylinder head. This has

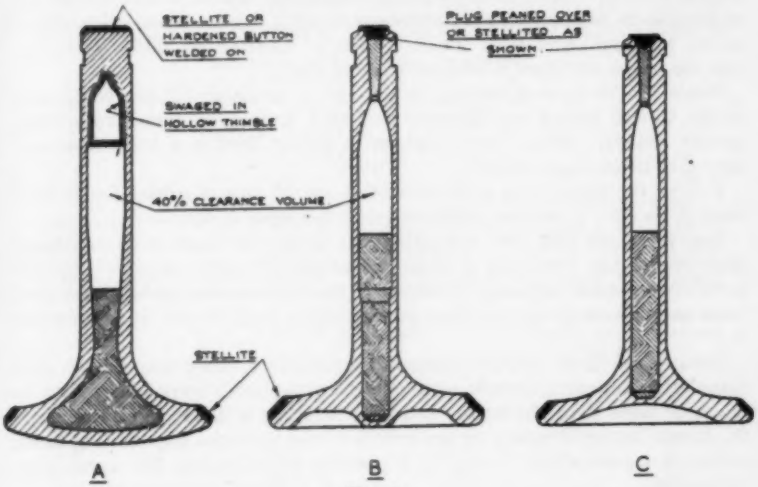


FIG. 3.

THREE TYPES OF SODIUM-FILLED VALVES.

proved quite satisfactory in practice, but I do not care very much for a hot valve, because it must eventually limit the engine performance, which could otherwise be obtained, by depreciating the anti-knock value of the fuel.

As engine performance is further increased I cannot help feeling that the hollow-head, fully cooled valve must be used. In some engines this will present a difficulty because of the seat distortion which is almost inherent in their design. The block type of construction, generally employed for liquid-cooled engines, is a typical example, and it is often more difficult to cure valve burning in this type of engine than in the case of a large air-cooled radial with separate cylinders.

Even the hot or "plastic" valve has been unable to cope with some types of cylinder head, because the head material itself becomes plastic in addition to suffering distortion; due to inadequate and uneven cooling and severe stressing. Fig. 3 shows some typical examples of sodium-filled exhaust valves in general use.

One of the principal requirements for the satisfactory operation of the exhaust valve is the necessity of making an exceedingly stiff and well-cooled cylinder head, so that there will be little or no distortion about the seat inserts. This will be of still greater importance if and when the fully-cooled valve is employed, because it has a greater degree of inherent stiffness due to its design, and also because it runs cooler.

Inserts of N.M.C.[7] steel continue to be used in this country, and this material is giving satisfactory service. Here again, the general practice, with few exceptions, is to stellite the insert seating in addition to that of the valve.

In this country, N.M.C. inserts are generally fitted in the cylinder-head by the screwing and shrinking method, and they do not usually work loose in service. But American and European experience is that it is almost impossible to obtain complete satisfaction with this material when shrink fitting the plain-ring type insert, which is common to those countries; and the insert will always become loose in time.

Steels similar in composition to that given in Table III are being used in the United States and Europe, and they have been found very satisfactory indeed. When the technique of fitting them has been mastered, they give little or no trouble.

I have for some time advocated the use of this material for inserts, since it also has a greater corrosion resistance than N.M.C.

The principal difficulty attending the fitting of these high-expansion steel inserts has been due to their rather poor thermal conductivity and lower coefficient of expansion, relative to that of the cylinder-head material. Consequently, they were at first given a fairly high degree of interference fit.

Because of their inferior thermal conductivity, they ran hotter than those of aluminium/bronze, and therefore probably expanded quite as much or more than the latter, and this, together with the big interference fit, caused severe stressing of the cylinder-head material surrounding them, giving it a permanent "set," and possibly overstressing the insert rings themselves.

Various types of inserts are shown in Fig. 4. Personally I favour (*c*) and (*e*) as good examples of the plain-ring variety, and (*a*) as a satisfactory screwed-type insert. The insert itself should be as rigid as possible under all conditions, and a heavy section ring used.

In a previous paper,[7] I advocated the use of the 45-degree seat for exhaust valves, and I am still of the opinion that this seat angle is the most satisfactory for all conditions of operation. But one cannot dogmatize on such matters, since the Wright "Cyclone" valve has a seat angle of 30 degrees and gives every satisfaction.

I think, however, the 30-degree seat is preferable for the inlet valve, since it gives a better average valve opening characteristic than one of 45 degrees.

The differential valve-seat angle is still employed by various manufacturers; that is to say, a valve having a seat angle differing from that of the insert, so that, when cold, it mainly seats on its large diameter. This has proved to be a satisfactory development in most cases. The included angular difference is generally in the region of 0·5 to 1·0 degree.

With regard to the particular matter of exhaust-valve and port design, I think it would repay the cost of investigation if some work was done to determine the effect of valve size and port shape on power. Because, if it were possible to use a smaller exhaust valve, it might give more scope for cooling it by improving the porting. Perhaps a venturi or so-called streamline-shaped port would be advantageous.

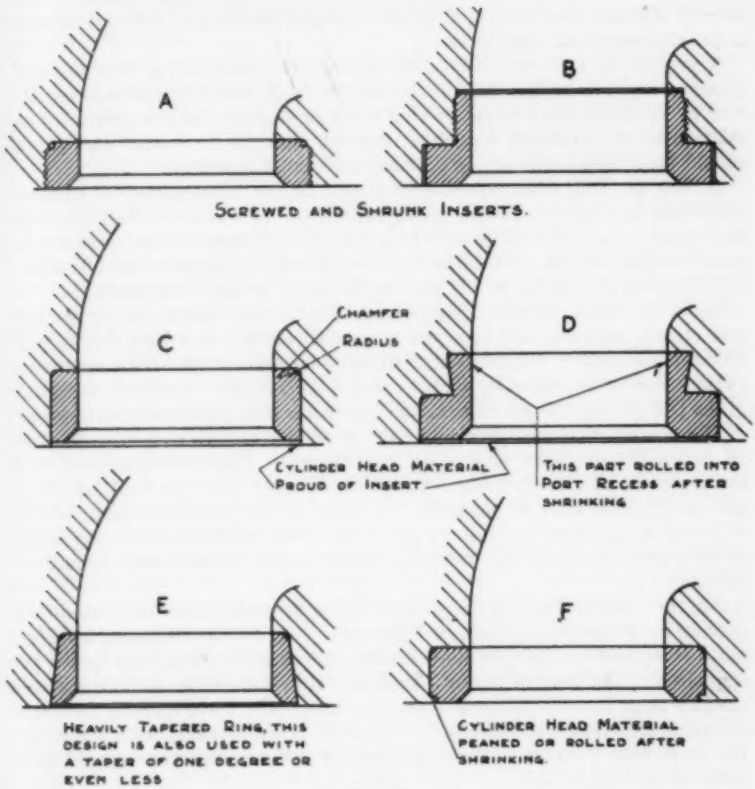


FIG. 4.

VARIOUS METHODS OF FITTING INSERTS.

A preliminary investigation along these lines was reported a few months ago in the *Journal of the Aeronautical Sciences* (U.S.A.),[8] but the investigators were mainly concerned with porting shape and efficiency, and not with heat dissipation.

It is possible that a large valve could be used with a relatively small lift, and the porting literally filled up with guide bossing in order to dissipate the heat rapidly.

The sleeve valve has so far shown no signs of hot corrosion attack, and

there have been no indications that this is likely to be a problem with this type of valve.

### Exhaust Pipes and Collector Rings.

Since temperature, particularly of the exhaust valves and exhaust arrangement generally, has a very definite effect on the rate of attack by the products of combustion of leaded fuel, the principal consideration in the case of exhaust manifolding is to see that, by its design, it keeps as cool as possible under all conditions.

A great deal can be achieved by fitting the manifolding in a suitable position relative to the engine (consistent with aerodynamic efficiency), and by ensuring that its internal volume or capacity is not restricted in relation to the cylinder capacity. Abrupt changes in volume and shape should be avoided as much as possible in exhaust systems.

In Europe, the usual material employed in the construction of exhaust manifolds has been mild steel, which, after forming, was welded and riveted. Mild steel is not the most satisfactory material for this purpose, and is very prone to split, due to a combination of temperature variation and vibration, which causes it to fatigue. It also scales badly at high temperatures.

Stainless steels of the ferritic, martensitic and austenitic types are now coming into use, and these are corrosion-resistant to a high degree, and do not scale easily. Stainless-steel exhaust collector rings, of the austenitic variety, are very generally employed by the military and civil machines in the U.S.A., and the use of mild-steel rings has been practically abandoned.

The class of material generally used is known as "18 and 8." That is, 18 per cent. chromium and 8 per cent. nickel. The carbon is kept to a low figure in this steel, being somewhere between 0·08 per cent. and 0·15 per cent. The steel is generally rendered stable for fabrication by the addition of either columbium or titanium; these reduce the susceptibility to inter-granular corrosion resulting from carbide precipitation caused by welding.

Another material which offers possibilities, and which has been tried with success for exhaust manifolds, is "Inconel." It has the following approximate composition: 80 per cent. nickel, 14 per cent. chromium and 6 per cent. iron. The fabrication of "Inconel" is said by some to be somewhat simpler than that of stainless steel, but those who have already had considerable experience of welding "18 and 8" prefer working with the latter, but state that "Inconel" does not usually suffer to the same extent from corrosion at the weld.

### Sparking-Plugs.

The production of a satisfactory sparking-plug becomes more difficult as the specific power output is increased, and now threatens seriously to restrict future engine development, although there should be no particular difficulty at the present time in choosing a suitable plug for flight purposes.

It must be appreciated, however, that the test-bed conditions to-day may be the normal flight conditions in a few years' time, and sparking-plug development does not seem to be keeping pace with engine development.

The principal plug troubles resolve themselves into two distinct classes. First, build up of lead deposits on the insulator causing deterioration of

the latter and electrical leakage if they fuse on to the insulator surface and remain hot; the fused deposits also tend to cause pre-ignition. Secondly, point burning due to erosion of the central electrode caused by the character of the electrical discharge and also the particular material used for the former. If a leaded fuel is employed, there is evidence, not only of erosion, but also corrosion of the electrode material by the combustion products of the fuel; since the rate of erosion of the electrode has often been found to increase by changing over from an ordinary to a leaded fuel under similar running conditions.

Deposit build up on the insulator is only really serious if fusing occurs, but if the temperature of the deposit can be kept below about 650° C., it is relatively harmless, and is even a reasonably good electrical insulator. It is most difficult to avoid the formation of fused deposits on plugs operating in high-duty engines. Even although a cool-running insulator may be designed, the layer of deposit immediate to the insulator surface will probably remain comparatively cool, but its outside surface will be swept by the hot combustion gases, which will bring about fusion.

The deposit coloration changes with temperature, having a greyish or yellowish tinge at the lower temperatures, to a dark brown or rust appearance at higher temperatures. On fusing, they generally become almost black and blistered in appearance.

The deposits formed on the plug insulator vary somewhat in nature according to the mixture strength and duty, but in general they are composed of the following constituents: lead sulphate, lead oxide and lead bromide. Lead sulphate is more or less innocuous, and is sometimes found to a greater or lesser extent when leaded fuel has been used, because however low the sulphur content of the gasoline, there is always sufficient to combine with the lead present to form measurable amounts of lead sulphate. It is, however, a fairly good insulator when cool.

The deposits are apparently somewhat hygroscopic or, if not hygroscopic, they hold moisture without necessarily absorbing it; particularly since the deposit provides an increased surface area of relatively rough or porous character in comparison with the original insulator surface. Enough moisture can be picked up or retained to cause difficulty in starting, and erratic running, which persists until the engine is thoroughly warmed up. In actual practice, however, this is not a serious trouble.

A high proportion of lead oxide, but little halide or sulphate, often composes the deposits on the insulator after high-duty operation. This would not normally be expected, but the likely explanation is that the lead bromide (the melting point of which is between 383° C. and 500° C., with a boiling point about 900° C.), when heated to temperatures around its melting point in the presence of oxygen and steam, is probably decomposed into hydrobromic acid and lead oxide, and would therefore account for the large amount of PbO which is found.

The lack of halide and sulphate may be explained by the fact that the lead is often present in the form of silicate, which is formed by reaction between lead oxide or lead salts and the silicates composing the mica insulation; although sometimes quite a high proportion (about 50 per cent.) of the deposit found on the cooler part of the plug inside the body or shell, consists of lead bromide.

In some engines the deposit has been found to vary in amount and somewhat in nature, from cylinder to cylinder. An increase in the amount of deposit is usually found in those cylinders which run with a slightly richer mixture than others, and occurs on the cooler running plugs.

Since the volatility of the fuel will influence the distribution, some research, which involves selective or fractional distillation of the fuel, would be valuable in order to ascertain how the lead is distributed in the fuel under these conditions.

There is little doubt that the combustion products of a leaded fuel amalgamate with, and attack, the mica under certain conditions, causing initial disintegration of the insulator surface. The degree by which the

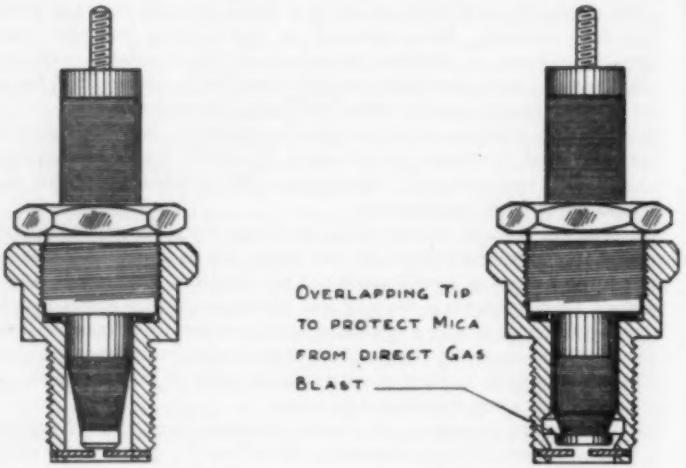


FIG. 5.
14-MM. LONG-REACH PLUG.

mica is affected is in turn controlled by the temperature of the deposit and the quality and surface finish of the mica itself. A high degree of surface polish of the mica will help in avoiding deposit attachment and attack.

In American sparking-plug practice a somewhat shorter insulator is employed than is normally the case in this country. This would at first appear to make the plug more susceptible to failure, due to the smaller leakage surface, but in practice this does not appear to be the case, and it is possible that the shorter heat path which is provided tends to keep the deposit cool, and therefore more resistant to electrical leakage.

The fact concerning the good insulating qualities of the deposit when kept relatively cool has been exploited with promising results. Fig. 5 shows a certain type of mica plug which, as in (*a*), was unsuitable due to deposit collecting at the upper end of the insulator and becoming hot enough to cause breakdown. The design of the insulator was then modi-

fied, as shown in (*b*), being made parallel for a large part of its length and tapered sharply towards the electrode tip. The restricted annulus between the parallel portion and the shell of the plug prevented free ingress of hot gases, and although some deposit formed there it remained relatively cool and non-conductive due to its proximity to the plug shell. That deposit which formed on the heavily tapered portion of the insulator near the tip was naturally somewhat hotter, but the relatively large clearance between it and the plug shell, together with the cooler deposit immediate to it, prevented electrical leakage.

During the last year or so a rather extraordinary trouble has been experienced; which is, the puncturing or "pin-holing" of the mica

FIG. 6.

insulation. An example of this is shown in Fig. 6, which is a photographic reproduction of an insulator after 20 hours of high-duty operation.

The puncturing is from the electrode of the plug outwards through the insulation, and often occurs remote from the electrode tip and about a third to half-way up the insulator. It would not be thought possible for leakage to take place at this point, where there is a relatively large space between the insulator and the shell of the plug, with a much smaller gap at the plug points.

An interesting theory has been put forward to account for "pin-holing," which is as follows: The ionization, which occurs before the discharge of the spark, is apparently very much influenced by the "atmospheric" conditions about the plug points. In other words, it is possible to deflect the ions between the plug points by a current of air or gas, so that they are more or less blown out of their direct course, and consequently the actual

resistance between the plug gaps is increased enormously. It is probable, therefore, that under these conditions the voltage in the plug builds up considerably, and, instead of the current discharging across the gap, there is some point inside the plug which, due to a fault in the mica, has a low enough resistance for leakage to occur. I am of the opinion that such leakage, producing puncturing, would not normally be possible if the mica were sound, and in all probability it is primarily due to faulty mica aggravated by the conditions at the plug points.

When visiting the United States this year the impression I gathered regarding sparking-plug failures was, that a large proportion were due to faulty construction and inferior mica, and not primarily to the use of leaded fuel. Undoubtedly the mica plug is not yet a back number, but it must be considerably improved to give trouble-free operation in the engines which are now being developed.

During the last few months, attention has been turned to a new insulator material in hope that it will provide a satisfactory solution to the troubles at present experienced. This material is aluminium oxide in the form of corundum, sintered to practically zero porosity. It is understood that, in its finished form, it is almost chemically pure aluminium oxide, no binders remaining in it after the manufacturing processes.

Sintered aluminium oxide was first produced by the Siemens Company in Germany, and it is marketed under the trade name of Sinterkorund.

Sparking-plugs having insulators of sintered aluminium oxide are also being produced by A.C., both in America and Great Britain, but only in an experimental way so far as aviation requirements are concerned.

Sinterkorund has excellent thermal conductivity, and it is impervious to attack by the products of combustion of leaded fuel. I understand that the principal difficulty with this material is that of obtaining uniformity of quality in production, and the sintering temperature is very high indeed, in the order of 1800° C.

It is as yet too early to say whether or not the sintered aluminium oxide insulator will be suitable for aviation plugs, but it certainly has properties which make it very attractive for use in the modern high-duty aviation engine. In addition to its immunity from attack by lead oxide at elevated temperatures and its relatively high thermal conductivity, it also has a specific thermal expansion which is closer to that of the electrode, particularly nickel wire, than the ceramics such as Sillimanite.

This is important because differential expansion between the electrode material, and the insulator has always been a disadvantage in the case of the usual ceramics used for this purpose, since it affects the sealing of the wire in the insulator and spoils the thermal contact.

Due to the nature of the material it is probably more difficult to fit a Sinterkorund insulator in the body or shell of a plug without risking a relatively high degree of gas leakage, and it is possible that the final development will take the form of a non-detachable plug.

This feature is not necessarily, in my opinion, a disadvantage, and it should be possible to make a more compact plug in this way. Such plugs can usually be cleaned by means of a sand-blasting equipment, and this method is commonly used, by service departments, for cleaning ceramic automobile plugs.

I think, also, that if these plugs prove successful and the manufacture of the insulator in quantity presents no difficulties, their production on a large scale will be possible at a relatively low price. In which case they can then be regarded more in the nature of a consumable store, and discarded when they become unserviceable due to erosion of the central electrode. It is hoped, however, that it will eventually be possible to have an electrode wire which will last for, say, 700 to 1000 hours, so that the plug can be serviced up to this period by adjustment or renewal of the earth wires.

So far as tests have gone in this country, there is one apparent difficulty, which is that of satisfactorily screening the plug for radio, and at the same time obtaining efficient dissipation of the heat which travels up to the terminal end, due to the superior conductivity of sintered aluminium oxide. Possibly, an increase in section of the tip and also the middle portion of the insulator which is fixed in the shell, leaving a small section or mass from this point to the terminal end, would allow a larger amount of heat to be dissipated to the shell and radio shield, if these were suitably designed, thus preventing overheating at the terminal end.

Coming to the sparking points of the plug, which include the central electrode and earth-wire assemblies, the principal requirements are as follows: A central electrode wire which will not erode or corrode, either due to the action of the electrical discharge or the products of combustion or to their combined effects. A material for the wire which does not cause a large increase in the working voltage, and finally, one which has a relatively good thermal conductivity.

The design of the sparking points should be such as to give low-voltage discharge. This generally takes the form of an annular gap or a series of gaps, in the case of a multi-point plug, which resemble a " broken " annulus.

Both the central electrode tip and the earth wires should be designed so as to provide a good heat gradient, from the tip to the electrode wire proper, and in the case of the earth wire, to the shell or body of the plug.

Too often is seen a large central electrode end, relative to the rest of the wire belonging to it, and there can be little chance of removing the heat efficiently from the tip. It is usual to force a copper tube or sleeve over the electrode, and up to the shoulder immediately behind the tip, but I often think that the thermal contact between it and the electrode material must be very poor indeed. In fact, in many cases it might be better to discard it and increase the size of the wire to about the same outside diameter as that of the sleeve, and obtain an improved heat flow in this manner. Perhaps, if the copper were cast around the electrode material and the whole drawn down to wire size, or if the copper were deposited on the wire by means of hydrogen brazing, it would then make a more satisfactory bond and do some good.

With regard to the question of gap burning, the design of the electrode tip and earth wires should provide for a good surface area over which the spark discharge can occur without concentrating about one spot. This avoids rapid erosion, and a good example of such a sparking-point design is that of the well-known B.G. plug, which is shown in Fig. 7(a).

Care must be taken, when adjusting this type of point, to see that the earth wires are set equidistant to the central electrode for the whole

sparking length. It is of little use to bend their ends towards the electrode tip only, since the spark discharge will then be concentrated at this spot and the rate of erosion increased.

Multi-points also assist in preventing a high degree of erosion because the spark discharge does not always occur between any one point, but is distributed between all.

A

THREE OR FOUR EARTHING WIRES ARE GENERALLY USED IN THIS CASE.

B

ANNULAR SPARK GAP - TWO OR FOUR HOLES ARE PROVIDED IN EARTHING PLATE.

C

FOUR POINT "BROKEN" ANNULAR GAP.

D

THREE OR FOUR EARTHING WIRES - RECTANGULAR IN SECTION - OVER A FLAT TOPPED ELECTRODE.

FIG. 7.

FOUR DIFFERENT TYPES OF AVIATION SPARKING-PLUG ELECTRODES.

A promising experimental plug has recently been produced by the K.L.G. Company. It consists of a flat-ended electrode over which are arranged, in radial form, six finely drawn platinum-iridium earth wires of about 0·020 inch in diameter.

This plug has proved very satisfactory in at least one type of high-duty engine, and has already shown that it will probably be capable of lasting out a type test of 100 hours' duration without attention; which is a considerable improvement over the present situation.

The earth wires eventually erode away, but until they show a high

degree of erosion they need little or no attention over relatively long periods, probably equivalent to about 200 hours under flight conditions. In connection with this erosion, it appears that the platinum is mainly removed, leaving the iridium. But it is a peculiar fact that pure platinum wires have been tried in some similar plugs, and have shown a higher degree of erosion resistance than the platinum/iridium wires, previously tested in the same engine.

It appears to be a peculiarity of some alloys that under certain conditions one of the elements is attacked, yet when used in its pure form it is reasonably satisfactory.

At first it would appear that such fine earth wires would give rise to pre-ignition, but in practice this is not so. Practical tests made by the K.L.G. Company have indicated that platinum/iridium wires of about 0·020 inch in diameter may be heated in a combustion chamber of an engine to a temperature as high as 1000° C. without pre-ignition occurring.

Whether or not these fine wires will be a solution of the erosion trouble remains to be seen, but a number of materials are now being tried, in wire form, to see if it is possible to obtain a higher degree of resistance to erosion.

One very important feature of the fine wire is that, due to its high operating temperature, it reduces considerably the working voltage of the plug, and so greatly assists in avoiding electrical breakdown, due to glazed deposit, and also pin-holing.

So far, no material has yet been found which is entirely satisfactory for use as a central electrode, but many have been tried, and a good deal of research continues to be done. Of those tried, the following materials have given fair results: nickel, manganese nickel, aluminium steel, tungsten, and austenitic steel.

Pure nickel appears to be one of the most satisfactory materials used for the sparking point of the central electrode, but it is generally employed in the form of a tip only, which is inserted in the electrode proper. This would at first appear to be unsatisfactory from the point of view of thermal conductivity, but in practice it seems to give no trouble in this respect, and tests have proved that the thermal conductivity is fairly good.

Most of the aviation plugs at present used employ an integral electrode and tip of austenitic steel. But this material has not been proved particularly satisfactory, except for that unexposed and insulated portion upon which the mica is first wrapped, and then over which mica washers are held in place under great pressure, putting the electrode in tension. Under these conditions austenitic steel has superior mechanical strength, and does not stretch. It appears quite satisfactory if a relatively large flat-ended electrode is used in conjunction with the fine-drawn type of earth wire, previously described.

Tungsten is unsatisfactory, particularly because it seriously increases the working voltage of the plug.

Reverting to the question of the nickel electrode tip, pure nickel is not satisfactory where fuels of high sulphur content are concerned, but this is not necessarily of importance, because the sulphur content of all aviation fuels is usually kept to a low figure, and normally no corrosion trouble due to this feature need be anticipated.

There is a further point with regard to the earth-wire assembly; the

earth wires should be well fitted in the plug shell to ensure good thermal contact. In this connection it is advisable either to braze or weld them to the shell. There is one disadvantage in brazing them, due to the fact that the brazing is liable to be attacked by the products of combustion, although this has not proved to be really serious in practice, since the plug usually outlasts any corrosion attack.

An interesting paper was written some years ago, by Watson,[9] on the question of spark gaps and voltage requirements generally. This is well worth while studying again, particularly in the light of recent experience.

British engines of the latest types are mainly using the 14-mm. plug in place of the previously popular 18-mm. size. The former has a number of advantages, such as low weight, which is important in the case of aviation engines employing two plugs per cylinder and having 9, 12, 14 and even 24 cylinders.

Also, it enables smaller bosses to be used in the cylinder head, and therefore allows considerable improvement in head cooling local to the plug; this feature is particularly valuable in the case of air-cooled cylinders, and if small cylinders are employed.

In my opinion the 14-mm. plug has one disadvantage, which is due to its small size; this is the difficulty of making satisfactory sparking points that can be easily and accurately adjusted. Also, the internal volume of the plug and the relatively small surface area of the insulator might make it more susceptible to failure, due to deposit formation.

However, one cannot say that its small size is an inherent disadvantage, because, so far, a number of other troubles have occurred which cannot yet be definitely blamed on the plug, and it is still largely in the experimental stage, despite the fact that its use is generally accepted for new engine types.

The plug reach and/or thread length has now more or less been standardized in this country. That is to say, for an 18-mm. plug the reach is 18 mm., and for a 14-mm. plug it is 14 mm. American practice was to have rather a short-reach plug, about $\frac{1}{2}$ inch, but this has now been modified and the reach increased to about $\frac{13}{16}$ inch in order to obtain a more satisfactory heat path.

Finally, as a matter of interest, I am reproducing below a copy of a laboratory report giving the analysis of the deposits taken from the insulators of some high-duty plugs which were fitted in an engine operating with a fuel of 87 octane, modified C.F.R. Motor Method, containing 4 ml. of lead per gallon:

"The central electrodes from two plugs were received, and each of them had a thin layer of brown/black fused material upon the mica body of the electrode.

"An approximate analysis is given below of each of these deposits:—

| | I. | II. | |
|---|---|---|---|
| Weight of deposit | 0·025 | 0·057 | grms. |
| Insoluble silica and silicates | 20% | 30% | (probably due to deposit removal by scraping the insulator surface) |
| Copper oxide | 4% | 6% | |
| Lead oxide | 60% | 40% | |
| Iron and aluminium oxides | 15% | 20% | |

"A little alkali is present in both cases.

"The actual weights of these deposits and also the siliceous material present are of little significance, as it was quite impossible to remove the deposit without at the same time removing some mica.

"No halide or sulphate could be detected in either case, and it seems probable that the lead is present in the form of silicate—formed by reaction between lead oxide (or possibly lead salts) and the silicates composing the mica. Mica varies considerably in composition, but consists chiefly of complex silicates of aluminium, iron and alkali metals.

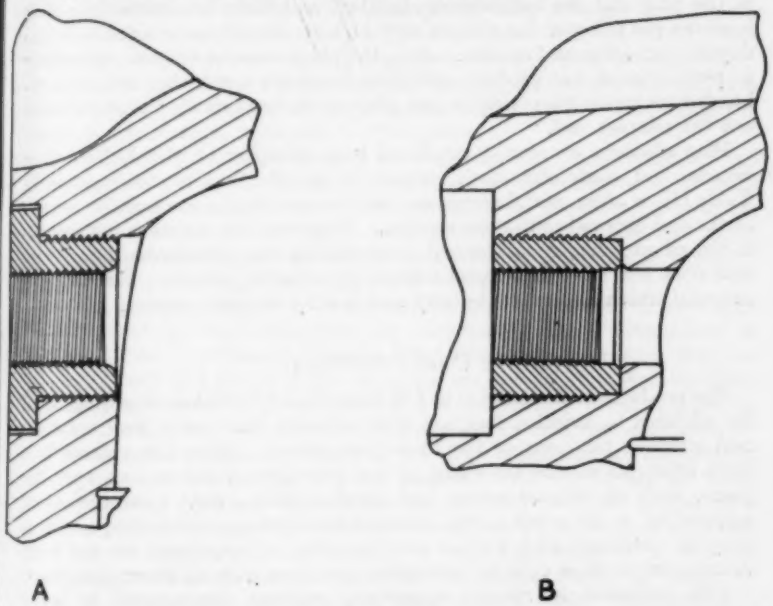


FIG. 8.
TWO DIFFERENT TYPES OF SPARKING-PLUG ADAPTORS.

"As regards lead silicates, at least eight varieties are known in which the ratio of PbO to $SiO_2$ varies.

"Lead silicates can be produced by the action of lead oxide on silica at temperatures in the region of 700° C. or slightly higher temperatures. They fuse readily between 700 and 800° C."

The design and fitting of sparking plug adaptors in the cylinder head should be given very careful consideration indeed, since satisfactory plug operation largely depends on this. In Fig. 8 I have given sketches which show two different methods of fitting the plug adaptor.

It is important to see that no screw threads are exposed in the combustion chamber, and sharp edges are to be avoided, and the entry from the combustion chamber to the plug should be made as easy and smooth as possible.

Modifications of the designs shown in Fig. 8 are in use, such as an adapter in which the plug is seated at its nose end immediate to the combustion chamber, instead of being screwed down against a copper washer on the outside of the adapter, which is the normal method of fitting. The object of this bottom-seating adapter is to obtain a better thermal contact between the plug and adapter than that which is normally possible through the threads.

Whilst this has been a fairly successful method of getting rid of the heat, it means that there will be a short passage between the sparking points of the plug and the combustion chamber, and there are indications that it allows gas to enter the plug at very high speed and cause trouble due to deposit formation and erosion. Also, the plugs must be finished accurately to provide good seat contact, and there is always a risk that some heavy-handed mechanic may tighten the plug up so hard as to distort or force out the adapter end.

Plug adapters are usually machined from phosphor or nickel/aluminium bronze, but austenitic steel, similar in specification to that given in Table III, is often used, because the bronzes are subject to corrosion attack at the end exposed to the combustion. However, this attack is not serious if the adapter has good thermal contact with the cylinder-head material and does not have any sharp corners or exposed threads. Inconel is a material which also might be very satisfactory for this purpose.

## Cold Corrosion.

The products of combustion of I–T Ethyl Fluid,[7] which is at present used for addition to aviation fuel, are lead bromide, lead oxide, lead sulphate and complex mixtures of the three compounds. These compounds and their mixtures can be the cause of hot corrosion of the various cylinder parts, such as exhaust-valves and sparking-plugs, etc. Cold corrosion, apparently, is the result of the bromine liberated in combustion, and this may be combined with lead as lead bromide, or may have reacted with aluminium or other cylinder materials prior to storage of the engine.

Cold corrosion in storage apparently requires atmospheric or other moisture to produce reaction with the bromine compounds and subsequent rusting and pitting, etc.

Cold corrosion is not now regarded as a really serious problem. This does not mean that such attack is not serious in itself, but rather, by employment of suitable technique, it can be alleviated to a large extent.

With regard to the actual attack of steel parts; some years ago in America there was considerable trouble with engines, due to the exhaust-valve stems being seriously corroded, causing their seizure in the guides. On starting, the rocker-arm boxes of the cylinders in question were often fractured, so tightly were the valves stuck or rusted. At that time in the United States valves of martensitic steel were in general use, and austenitic steel had not yet been employed for this purpose, although British manufacturers had been using it for some time.

Cobalt-chrome was a particular offender in this respect, and had very low resistance to cold corrosion attack. The austenitics are highly resistant, and are not normally attacked in this manner. Therefore, when con-

sidering treatment to avoid cold corrosion, the cylinder barrels are the principal parts to receive attention in the modern engine, not the valves, and the latter can be practically disregarded.

Outwardly, this attack generally appears to be much worse than it really is, and although there is seen a brown paste or slime, resembling iron oxide mixed with oil, on the cylinder walls, this can generally be wiped off quite easily, and often little or no etching of the barrel is apparent.

Cases occur every day where, if one looked inside the cylinders before starting an engine, one would refuse to believe that it could operate satisfactorily because of the apparent signs of corrosion present; but there is no doubt that many engines frequently work under such conditions which in certain circumstances occur during very short periods between runs.

Sometimes an engine will be stored for months without trouble, and then a combination of temperature and absolute humidity will occur, which will cause corrosion to be apparent in a few hours.

Provided that the cylinder walls are well lubricated, the attack will not cause serious pitting of the steel, even if left without attention for some time. If provision could be made to introduce oil, from the low-pressure lubrication system of the engine, into the cylinders via the inlet valve ports, at low throttle openings and just before stopping the engine, probably very little trouble would be experienced in service.

So far as those engines are concerned which are installed in civil type aircraft used by the airline-operating companies, special precautions do not appear to be necessary, because when they are not working they are generally only laid up for a day or so, or are due for overhaul, in which case they will be in a dismantled condition. Therefore, it is not usual for an air-operating concern to treat their engines for cold corrosion attack.

The most difficult cases to deal with are those of the military air services, where very much less flying is done compared with the regular air lines; a machine may fly for an hour or two one day and be in the hangar for a week or more. To counter possible troubles in this connection it is suggested that an oil injection device, similar to that mentioned in a previous paragraph, be used, in addition to which the engines should be turned by hand, at the propellor, about two or three times a week. This procedure is recommended, whether or not leaded fuel is used.

Admittedly, the addition of a further accessory to the modern engine is not desirable, because there are more than enough already, and if an injection device cannot be fitted, it may be necessary to inject oil, or a specific anti-corrosion material, into the cylinders through the sparking-plug holes.

Oil alleviates the trouble, but does not entirely prevent corrosion attack. In this connection a very effective anti-corrosion material, known as "E.G. 174," has been developed by the Ethyl Gasoline Corporation for the treatment of engines before they leave the manufacturers' works, and so that they can be stored for prolonged periods. In addition, it is also intended for those engines which are stopped for indefinite periods, similar to the conditions previously described for military machines.

This material is the result of many experiments covering two years or more, and it is the most effective mixture so far produced for the prevention of cold corrosion. It is composed of the following constituents :—

TABLE IV.

| | | |
|---|---|---|
| Triethanolamine | = 5/6% | by weight |
| Normal Butanol (Butyl alcohol) | = 10/12% | ,, ,, |
| Aluminium Stearate | = 10% | ,, ,, |
| Lard Oil | = balance | |

A full description of it and also a manufacturing specification is given in Appendix II at the end of this paper. No patents have been applied for "E.G. 174," and those who wish are free to prepare it themselves, or have it made up by competent manufacturing chemists.

We have been asked, from time to time, whether it would prevent cold corrosion attack if engines were run on clear gasoline, without lead, before stopping them; and although this helps matters somewhat, it is not a cure. However, an engine, immediately after test, should be operated on clear gasoline before being finally removed from the test bed, after which the cylinders, and any other parts, should be sprayed with the "E.G. 174" mixture.

A special type of spray gun for dealing with viscous materials has been developed for the Ethyl Gasoline Corporation by the DeVilbiss Company. This gun is used for the application of "E.G. 174," and it is especially adapted for spraying the cylinders through the spark-plug holes (See Appendix II*b*). The engine crankshaft is rotated after each cylinder is sprayed, in order to ensure that all cylinders are completely treated.

The use of materials treated by the nitrogen-hardening process has been queried so far as their corrosion resistance is concerned, but experience in Great Britain and in Europe indicates that, so long as nitrided parts are kept well lubricated, little or no trouble need be anticipated. A great deal depends on the particular materials nitrided, but parts such as cylinder barrels, and particularly sleeve valves, can be considered quite satisfactory in this respect. The normal type of poppet valve may be nitrided on the stem for the full guide length, but the nitriding should not extend beyond the guide into the exhaust port, when the valve is in the closed position.

Chromium plating of such parts has been tried in order to prevent corrosion attack, but so far little progress has been made; mainly because of the difficulties attending the successful deposition of the chromium so that it will adhere and not flake off.

## LIGHT ALLOY FUEL TANKS AND LEADED FUEL.

Some queries have arisen regarding the effect of leaded fuel on the materials used for aircraft fuel tanks. No trouble has been experienced in the case of tanks manufactured from the usual aluminium alloys, but with regard to those particular alloys which contain a large percentage of magnesium, such as "Elektron," corrosion would be experienced if certain precautions were not observed.

The experience to date is, that corrosion trouble is experienced with high magnesium alloys when free water is present with the fuel, whether the latter contains lead or not. If it contains lead, then the corrosion attack is considerably accelerated. From this one deduces that the presence of water is really the governing factor, but it is almost impossible to avoid a certain amount collecting in fuel tanks. I suggest, however, that magnesium alloy tanks could be designed with provision for a large sump of

some material which does not suffer from this corrosion attack, such as aluminium, etc. The sump would be of such size and design as to prevent any water reaching the joint between it and the tank proper, in order to avoid the possibility of electrolytic action. It could be fitted to the tank with stainless-steel bolts, and "langite," or similar material, used to make the joint between the two.

A good deal of research has, however, been done during the last three or four years in order to combat this particular corrosion attack. Work has been carried out, separately, by the R.A.E. at Farnborough, the I.G. Farbenindustrie in Germany, and the Ethyl Gasoline Corporation Laboratories at Detroit.

The I.G. was the first organization to find a successful method for preventing the corrosion attack of magnesium alloy fuel tanks. This concern developed a perforated magnesium alloy "cartridge" containing a small fabric bag filled with potassium or sodium fluoride. The complete "cartridge" was then screwed into the base of the fuel tank, in direct contact with the fuel. Sodium fluoride has been mainly used by the I.G. for this purpose, but it does not appear to be effective unless the magnesium alloy tanks are first treated by the I.G. process for the general protection of these alloys; this involves dipping them in a chromate/nitric acid bath, which produces a protective film on the surface of the metal, but removes some of the material in the process. After this preliminary treatment, however, the sodium fluoride "cartridge" appears to give excellent protection. Sodium fluoride is soluble in water, but not in the fuel, and, also, it does not seem to have any harmful effect on leaded fuel. There is some question as to whether aqueous sodium fluoride solution, which is produced as the result of water being present in the fuel tank, will tend to cause serious corrosion trouble with any aluminium alloys that may be used in other parts of the fuel system. This matter is now being investigated.

The R.A.E. has done a large amount of work over two or three years, and has developed a similar cartridge-type corrosion inhibitor to the I.G., but with a different compound—namely, zinc chromate. This compound is apparently even more effective than the fluorides used by the I.G.; almost complete protection appears to be afforded to magnesium tanks containing large amounts of water in the presence of leaded fuel of high concentration, and although the preparatory chromate treatment of the tank is advisable, the compound gives a high degree of protection without it. In addition, it is much less water-soluble than sodium fluoride and, therefore, is not so liable to cause trouble due to deposit formation in other parts of the fuel system. Strontium chromate is also very effective as a corrosion inhibitor.

A "cartridge" or pellet has been developed by the Ethyl Gasoline Corporation which consists of calcium chromate which is fluxed with borax in the proportions of two parts of borax to one part chromate; in this case no preliminary chromate pickling of the material is necessary. This pellet appears also to supply an answer to the corrosion of magnesium tanks, and the results of prolonged tests have shown it to be exceedingly effective.

The three above-mentioned methods of protection are apparently similar in principle, in that they depend on the formation of a protective coating

on the metal surface. Sodium fluoride is very soluble in water, which means that the cartridges have to be replaced at frequent intervals. A large number of chromates are known, ranging in solubility from the very high solubility of the alkali dichromates down to practically complete insolubility. The choice of a suitable material will depend then on the determination of the minimum concentration of chromate ions which will

FIG. 9.

SKETCH SHOWING APPLICATION OF CORROSION INHIBITORS TO AIRCRAFT FUEL TANKS.

[*Note.*—30–40 grams of the fluoride will be sufficient to treat a tank of approx. 100 gallons capacity for over one year.]

afford satisfactory protection. The sparingly soluble chromates, such as those of zinc and calcium, are satisfactory, according to the above investigators. It would seem, therefore, that one of their advantages over fluorides is that a given amount of material would give protection for a period roughly inversely proportional to its solubility. In Fig. 9 is shown the method of fitting the cartridge, containing the corrosion inhibitor, to aircraft fuel tanks of high magnesium alloy.

## FURTHER PROBLEMS RELATING TO THE APPLICATION OF HIGH OCTANE FUELS.

So far, I have discussed the question of cylinder-head design and valve arrangement, and also those points particularly affected by the use of leaded fuel and its combustion products, regardless of the anti-knock value of the fuel. But I now propose to deal with those matters which are particular to the development of engines to use 87 and 100 octane fuels.

Future engines employing these fuels, more particularly the latter, can be developed along two distinct lines; first, for those military or civil machines of short range, where fuel economy is relatively unimportant and a high degree of boost or supercharge is required to obtain the maximum power possible for rapid climb or take-off with large loads and, perhaps, from small aerodromes. Secondly, for long-range work, for bombers and civil machines having to operate between far-distant points, where fuel

economy is of the greatest importance and where the maximum power may have to be sacrificed for a low fuel consumption.

Disregarding the military aspect for the moment, since fuel cost is not necessarily a primary consideration in this case, I think that the use of 100 octane fuel will be well worth while for the short-range civil aircraft, because even if it costs, say, three times the price of 87 octane fuel, the increased power available for take-off, by means of high boost and moderate compression ratio, will allow a greatly increased pay load to be carried, and more than compensate for the extra fuel cost. Some indication of the possible operating economy on 100 octane fuel has been given by Bass in the papers referred to.[10]

It has been suggested, however, that although a higher power can and will be made available for "take-off," by the use of 100 octane fuel, there may be certain limitations where a two-position variable-pitch airscrew is used, which will prevent maximum r.p.m. being developed under low-forward-speed conditions. That is to say, for an engine of given rated power it may be difficult to increase the maximum or "take-off" power beyond a certain percentage of the normal rating, because the controllable pitch airscrew will not give a wide enough range for the best "take-off" characteristics and also be efficient at the normal cruising power of the engine. For a constant-speed airscrew, however, these limitations should not be so effective, but much will depend upon the airscrew designer to convert this power increase into thrust.

Data are already available to show that it is possible to increase the power of a given engine by about 30 per cent., due to the greater degree of supercharge permissible with 100 octane fuel. (Refer to Appendix I.)

So far as the engines for long-range machines are concerned, these will probably employ a high-compression ratio and a relatively low supercharge or boost pressure, and although it is here that 100 octane fuel will show to great advantage, such engines will present very definite difficulties in development if really low fuel consumptions are to be obtained.

Assuming all other conditions to be unchanged, and with no detonation or pre-ignition present, an increase in compression ratio will improve power output and lower the specific fuel consumption. It will also reduce the specific and total heat rejected to the cooling medium and exhaust gases. Unfortunately, however, an increase in compression ratio is more severe on the fuel and engine (except the exhaust valves) than an increase in boost pressure, and in order to obtain a substantial reduction in fuel consumption, it will be necessary to raise the ratio to about 7·75/1 or 8/1, from the present average of about 6·4/1.

This will, in turn, give rise to considerably increased maximum combustion pressures, in the neighbourhood of 1000 lb. per sq. in. for a ratio of about 8/1; being equivalent to a momentary load of about 12·5 tons on a piston head of 6 inches in diameter.

It is to be regretted that there are as yet no reliable engine indicators which will record accurately the maximum pressures, the rate of pressure rise or the rate of change of pressure, in the cylinders of a high-duty engine.

I am aware of three promising cathode-ray indicators which, I hope, will soon be able to provide the engine manufacturers and the fuel suppliers with this information. These are: the Metrovic-Dodds, the Cossor, and

the Standard Sunbury. Two of these instruments can also indicate the rate of change of pressure, which is of particular importance when estimating the effect of gas loading on the engine parts.

Reverting to the question of high compression ratio, undoubtedly the principal factor to consider is its effect on the durability of the various engine parts such as the cylinder head, the cylinder holding-down studs, the piston and connecting-rod assembly.

These will have to be considerably strengthened and stiffened up in many cases, particularly the pistons and cylinder heads, which must be of sufficient strength and rigidity to withstand such pressure loadings without fracturing or flexing.

It is often assumed that, because the Air Standard Efficiency curve flattens out considerably at the higher compression ratios, it is not worth while increasing the ratio above, say, 8/1. Whilst there are apparent mechanical difficulties, which make even an 8/1 ratio appear somewhat high for safety at the present moment, the higher the ratio which can be employed, the greater the degree of inherent fuel economy it is possible to obtain. It is questionable, however, if a higher ratio than 8/1 can be used, without a considerable increase in weight of structure, although it may be possible to do this and still keep the weight well below that of a C.I. engine, for very long-range aircraft.

One of the principal difficulties with the gasoline engine, is to reproduce, in flight, those fuel consumptions obtained on the test bed. Whilst specific fuel consumptions from 0·34 to 0·40 lb. per b.h.p.hr., according to the type, are practically inherent in the compression-ignition heavy-oil engine, some complication, such as automatic mixture and altitude control, and also ignition control, is necessary for the gasoline engine in order to get anywhere near test-bed figures in flight.

However, it is only a matter of time before the very low fuel consumptions, which have already been obtained experimentally, will be attained in flight, and the high take-off power and low weight now possible with the gasoline engine have already somewhat retarded the development of the C.I. engine so far as aviation is concerned; although, naturally, it would not be wise for the protagonists of the former to rest on their laurels.

Having in mind the performance of the racing Napier "Lion" of 1927,* I do not see why a specific fuel consumption of 0·35 lb. per b.h.p.hr. should not be possible in a few years' time, for flight cruising conditions. It may be necessary to develop a supercharger which will give, with the aid of intercoolers, a relatively low temperature boost for take-off purposes and, on reaching cruising altitude, the supercharger drive will then be completely disconnected from the engine, to avoid mechanical and blower losses.

Since the amount of load which can be carried in flight is determined by that which it is possible to take off the ground, the take-off horse-power is the most important factor governing the operating economy of an aeroplane. A year or so ago it would not have been possible to utilize a high proportion of the power available in the engine for take-off purposes, because of the fixed pitch airscrew, the blades of which had to be set at an angle which allowed the engine to give maximum power and r.p.m. at rated altitude; therefore, limiting the power for take-off.

* This engine also had a high mechanical efficiency.

Now, however, the general use of the controllable pitch, and also a later development, the constant-speed airscrew, allows a large proportion or the maximum power to be used for this purpose, and the take-off run can be enormously decreased or, conversely, a much greater load lifted off the ground, without an unduly long run.

It has now become essential to quote three power ratings for a given engine, so as not to restrict the aircraft designer and to enable him to make the best possible use of the power available. In the past insufficient information was available to him when only one power was given, which was the maximum power at maximum r.p.m. at rated altitude, level flight; or, in the case of the international rating, maximum power at normal r.p.m. These three ratings may be tabulated as follows:—

(1) *Take-off Power.* The maximum power at sea level at which the engine will operate with the maximum permissible boost, without detonation. This power is not available for continuous operation, but, generally, only for five minutes, or until the power falls off to that of the normal rating of the engine, as altitude is gained; whichever period is the less.

(2) *Maximum Power.* The maximum power at maximum r.p.m., or sometimes normal r.p.m. (international rating), in level flight and at rated altitude; for limited operating periods.

(3) *Cruising Power.* This is usually the maximum power at which the engine may be run continuously at normal r.p.m., and with a guaranteed minimum fuel consumption.

## Maximum Power Production.

For the production of high power, where fuel consumption is not of primary importance, much depends on the supercharger and its efficiency.

Whilst it is now possible to gain 30 per cent. or more in specific power output with 100 octane fuel, as compared with a fuel of 87 octane, there are certain difficulties which must be overcome if it is desired to use the fuel to the greatest advantage.

One of these difficulties pertains to the high boost temperature which is now common with the modern big-capacity high-altitude blower. Boost air temperatures in the order of 120–130° C. are becoming quite usual, which, allowing for the effect of the latent heat of the fuel, gives a charge temperature of 100° C. or more.

Experiments made on liquid-cooled, full-scale engines have indicated that a difference of 30° C. in the boost air temperature was equivalent to a gain of about 20 lb. per sq. in. b.m.e.p., in favour of the lower temperature. In this case the range was from 70° C. to 100° C.

This gain varied in magnitude with fuels of different composition; those of relatively high aromatic content showed an even greater increase at the lower temperature in these particular engines.[11]

Whilst it would be unwise to take too much for granted as a result of these tests, at least until further work has been done, sufficient evidence is available to show that high boost temperatures seriously affect the anti-knock value of the fuel. The loss of 20 lb. per sq. in. b.m.e.p., due to

a temperature rise of 30° C., may mean a difference of 100–150 b.h.p. or more in the case of a full-scale engine of about 1000 b.h.p. That is to say, if the boost air temperature could be lowered by means of intercoolers to 70° C., the engine could possibly be rated at 1100–1150 b.h.p.

Intercoolers appear to be necessary to the modern engine, but there are a number of complications attending their use. At the moment there are no published data to show whether or not an efficient intercooler is yet in existence and, if so, whether it absorbs too much power in the form of drag.

A further point regarding the adoption of an intercooler is that, on practical consideration, it may have to be used in conjunction with a pressure-type carburettor. That is to say, it will probably have to be placed on the pressure side of the supercharger, and between it and the carburettor, because a homogeneous mixture could not be maintained if the fuel had to pass through the intercooler, and, also, there is the risk of serious damage if an explosion occurred due to firing of the charge in the induction system.

Whilst this arrangement has the advantage of eliminating carburettor icing, which is a considerable worry to airline operators at the moment, it probably means that there will be some drop in supercharger efficiency, due to the fact that the fuel does not pass through the blower, and thus the beneficial effect of its latent heat is lost; although this appears to be inevitable if an intercooler is fitted.

The pressure carburettor system is exceedingly difficult to arrange in the case of the air-cooled radial, and would complicate matters considerably at the rear end of this type of engine.

The two-speed supercharger is possibly an immediate alternative, pending the development of the intercooler, since it reduces to some extent the power loss and boost temperature at take-off condition, where at least a reduction in the latter is most beneficial and desirable.

The two-stage blower with an intercooler and carburettor between the stages is yet another arrangement, but the exhaust driven turbo-supercharger with intercooler and pressure carburettor is probably the ultimate goal. The principal advantages of this scheme are, that not only is the icing trouble disposed of, but a practical and relatively simple automatic boost regulation is also provided.

A considerable amount of work has been done in the past on gasoline injection by the U.S. Army Air Corps, and although this body has encouraged outside firms to develop injection systems, nothing so far appears to have materialized in the way of a standard production engine having this system.

It is suspected that the principal reasons why it has not been more fully exploited are mainly those concerning cost and complication. The cost is, apparently, very high indeed relative to that of a carburettor, and is in the order of five to six times as much.

As far as complication is concerned, it appears difficult to make pumps on a production basis which will meter accurately, although it is not easy to see why this should be more so than in the case of a fuel pump such as the Bosch. Apparently, the main difficulty is in co-ordinating the injection and the air control satisfactorily.

There are three principal methods of injection which can be used:

(*a*) by means of an injector fitted directly into the cylinder head, (*b*) injection into the induction pipe, and (*c*) injection into the eye of the blower.

The first, (*a*), complicates the cylinder-head design and adds another boss to it, which is undesirable, although it may assist in direct cooling of the cylinder by means of the fuel.

The second, (*b*), is quite satisfactory, but since air only is taken into the supercharger, loss of efficiency is incurred.

The third, (*c*), not only avoids icing trouble, as is also the case with the two previous methods, but it does not impair the blower efficiency.

Mock,[12] who is one of the leading authorities on gasoline injection, has stated in a recent paper that he believes the injection system must eventually be used.

Both air- and liquid-cooled engines are in production to-day, giving more than 1000 b.h.p. for cylinder capacities between 27 and 30 litres (1650–1830 cu. in.) and using 87 octane fuel. This is eqivalent to b.m.e.p.'s in the order of 175 and 200 lb. per sq. in., maximum.

Employing 100 octane fuel, this power could be increased to about 1200–1400 b.h.p., but blower limitations may seriously restrict the possibilities of obtaining still larger power increases at rated altitude from a given cylinder capacity, or swept volume.

In the case of a highly supercharged engine, developed for maximum output, it is often undesirable to attempt also to increase the compression ratio; because, apart from the question of high gas loading, the power may actually be reduced, due to the fact that the compression space above the piston is made smaller in volume, and thus reduces the weight and volume of charge which can enter.

Naturally, there will be an optimum compression ratio for every engine, below which it will not pay to go on account of fuel economy, but an investigation should always be made to determine the optimum conditions for boost in conjunction with compression ratio.

I well remember some supercharged racing-car engines which had too high a compression ratio for their boost. Decreasing the ratio by one half of one unit increased the power by about 8 per cent.

Klein,[13] in another valuable paper, gives further data on the work which has been done by the U.S. Army Air Corps on 100 octane fuel.

## Minimum Fuel Consumption.

Engines designed to give the best fuel economy may have a somewhat higher structure weight than those developed purely for high-duty operation, for the reasons previously stated.

One of the leading engine designers in this country has stated that the specific fuel consumption could be reduced by about 0·04 lb. per b.h.p.hr. by the use of 100 octane fuel in relation to one of 87 octane. However, I think that an even greater reduction is possible if an engine were designed specifically for this purpose.

The present cruising fuel consumption which is obtained by a number of European aircraft-operating companies is in the region of 0·48–0·50 lb. per b.h.p.hr. on 87 octane (C.F.R. Motor Method). Undoubtedly this could be somewhat reduced on the same fuel, but due to the fact that a

number of the routes are relatively short it probably does not pay to have a much lower consumption, particularly since there has been no device available until recently to give the pilot an accurate indication of the safe mixture strength he can use.

About a year or so ago, the American branch of the Cambridge Instrument Company produced an exhaust gas analyser particularly designed for use in aircraft. This is now extensively employed by the aircraft-operating companies in the United States and by the K.L.M. and, I believe, Swissair, in Europe. It is a modification of their well-known $CO_2$ recorder.

This instrument records the mixture strength as determined mainly by the relative hydrogen and to a lesser degree the $CO_2$ content of the exhaust gases, and the sampling element is placed in the exhaust system of the engine, with an indicator provided in the pilot's cockpit. The scale of the indicating unit is suitably graduated and divided into safety and danger zones. The pilot is then able to lean the mixture fairly accurately to within safe limits, and to a figure predetermined by the engine manufacturers. A description of the indicator and its installation in an aircraft is given by Young [14] in the paper referred to at the end.

The "Cambridge" has one important disadvantage, which will become apparent when the specific fuel consumption is reduced to a point that represents the theoretically correct mixture strength, or weaker.

Its operation largely depends on the thermal conductivity of hydrogen, which is present in the exhaust gas at all mixture strengths richer than the theoretically correct ratio. Therefore, on reaching this ratio, and with the reduction and elimination of the hydrogen, the instrument will give inaccurate recording.

It will, therefore, be necessary to re-calibrate it, and to employ another constituent of the exhaust gas, when working at, or below, the theoretically correct air/fuel ratio.

In the latest model of the "Cambridge," instead of being graduated in terms of mixture strength, the scale is marked off in increments of boost pressure; so that the pilot sets his engine to run at a given boost, and then adjusts the mixture control to give the same figure as the boost, on the "Cambridge" scale.

A further detailed description of this instrument is given in the *Journal of the Royal Aeronautical Society* for November 1936.[15]

The "Cambridge" equipment is generally employed for the Wright "Cyclone" engines in airline operation. The engines produced by the Pratt & Whitney concern do not, however, appear to make use of this instrument, but depend on the automatic mixture control carburettor for accurate mixture setting to obtain low fuel consumption. This carburettor is said to be very satisfactory, and does not appear to give any trouble when adjusted properly in the first place.

Certain of these engines, fitted in long-range aircraft, are operating with a specific fuel consumption of 0·43–0·44 lb. per b.h.p.hr. on 87 octane fuel. Even although the cruising horse-power may be only 50–55 per cent. of the available take-off power, this consumption is extraordinarily good.

I think it reasonable to suppose, in the case of an engine specifically designed to use 100 octane fuel, having a high compression ratio, approaching 8/1, and moderate or low boost, that a fuel consumption of 0·38 lb. per

b.h.p.hr. is immediately possible; and even lower figures, say 0·32–0·35, will be obtained in the not too-distant future, for cruising conditions.

Young,[14] in his paper, gives an extraordinarily low fuel consumption of 0·34 lb., but since this figure represents only the lowest point on a consumption curve it is improbable that the engine concerned would operate continuously at such a figure.

The American type air-cooled radial engine has shown that it can operate at a relatively low fuel consumption, and one of the reasons advanced to account for this is as follows: For a given power output and cylinder capacity, the American engine usually runs at lower piston and crankshaft speeds than similar British types. Therefore, for the same power in both cases, the b.m.e.p. of the American engine will be somewhat higher. For a given engine and a fixed power output, fuel consumption is a function of speed, and consequently an engine should have a lower specific consumption if it is run at maximum m.e.p. conditions, which means that the crankshaft speed will then be reduced for a predetermined or fixed power output.

The mechanical losses will be less if the operational speed is lowered and, for a similar reason, the blower losses may also be reduced; although, in the latter case, so much will depend on the blower itself and the particular conditions for which it is designed.

There are probably other reasons to account for this variation in fuel consumption, and a number of exceptions exist; but no work has yet been done to determine all the causes accounting for this difference between the engines of the two countries.

A further point, which may favourably influence the fuel distribution and consumption, is the arrangement of the induction pipes from the blower to the cylinders. In the case of American engines these are usually taken tangentially from the blower-casing, whereas British practice has been to lead them approximately radially from the blower casing.

Speaking of carburation generally, there are indications that it is better, where possible, to employ a carburettor having a single large choke, rather than one having a multiplicity of smaller chokes. Since, for a given area, the former reduces the orifice losses somewhat, and helps to increase the efficiency of the blower by improving its inlet side. Also, the large choke may tend to make the carburettor less critical to icing, because of the lower percentage restriction offered under these conditions.

Whilst there are certainly advantages in the particular lines of development adopted by the American manufacturers, it is felt that the low-speed engine, with large cylinders working at relatively high b.m.e.p., is more critical to fuel quality (anti-knock value) than the equivalent British types. Modern British engines are producing similar take-off powers to American engines, with somewhat smaller cylinder capacity and with a fuel which, on the average, is two octane numbers less than that generally used in the United States for the same purpose.

An important matter, about which little has yet been done, is that of the automatic ignition control. Actually, the automobile manufacturers are ahead of the aero-engine people in the development and use of this device, but this is mainly because of the varying load operation of the automobile engine. Automatic ignition control is of great advantage, particularly

in so far as weak mixture operation is concerned, where a greater degree of advance than normal is usually necessary.

A further important point to consider with regard to ignition and satisfactory engine operation, is that of sparking-plug position. Whilst I have previously mentioned that the best positions for the plugs should be determined, if necessary, by practical tests with different cylinder heads, it has been found that it is not always desirable to place either one, or both sparking-plugs, local to the exhaust valve. Often, when they have been fitted close to the valve, trouble has been experienced with both valve and plugs, in some high-duty engines.

The plug either becomes overheated due to the proximity of the valve, and causes localized detonation or pre-ignition, which in turn overheats the valve edge; or, conversely, it may be that when the plug fires and ignites the charge, hot gas is projected on to that side of the valve nearest to it. This heats up the valve, which in turn may eventually cause overheating of the plug. A further reason is, that by placing the plug bosses near to the exhaust port, distortion may occur, due to changes in the material section, and inferior cooling. This will in turn spoil the gas seal between the valve and its inserted seat, and cause overheating of the former.

In some cases, by removing the plug, or plugs, further away from the valve, both actual valve burning and plug trouble have been cured, without any apparent or harmful effect on combustion efficiency.

## General Discussion.

The criterion by which an automobile engine is often judged is its specific power, or power per litre of piston displacement, at full throttle. Although high specific power is desirable in the case of the aero engine, the latter should not be judged solely on this basis.

Aero engines have been produced which give high power relative to the piston displacement, but are somewhat heavy and have a high fuel consumption. It is exceedingly difficult to suggest the most suitable cylinder arrangement and size for the best power/weight ratio and fuel economy, but two papers, by Fedden [10] and Wood,[11] to which I have referred, give some suggestions on the design of future engines.

Broadly speaking, I think the large cylinder of about 6 inches diameter and 3 litres capacity probably provides better optimum conditions for power, weight and fuel consumption than does a smaller cylinder having, say, a capacity of 1 litre; but the former will most likely be more fuel-sensitive than the latter. Therefore, as a compromise between the two sizes, a cylinder of 1½–2 litres capacity might be better.

However, since the frontal area and the form of the engine are of great importance, the final cylinder arrangement will rather depend on the duty for which it is intended.

At present there are four main types of high-duty engine in use to-day: (1) the liquid-cooled twelve-cylinder V type; (2) the air-cooled radial of nine cylinders; (3) the air-cooled two-row staggered radial of fourteen, and even eighteen, cylinders; (4) the air-cooled H engine of twenty-four cylinders, with two rows of six in-line side by side, upright, and two rows inverted, on two crankshafts; with the airscrew reduction pinion between the two crankshaft pinions.

It is possible that types (1) and (2) will eventually be developed to give take-off powers of about 1200–1400 b.h.p., with cylinder capacities between 27 and 30 litres; and type (3), 1400–1800 b.h.p. for 40 or 45 litres. The H engine, so far, has only been produced in small cylinder sizes having about 16–17 litres total swept volume, but it gives a relatively high power of over 700 b.h.p. In its present form, however, it is somewhat heavy, despite its high specific power.

For *rated* powers of 1500–2000 b.h.p. some different arrangement may be necessary, and up to twenty-four cylinders used. The swept volume will mainly vary according to the power requirements, and also to the type of

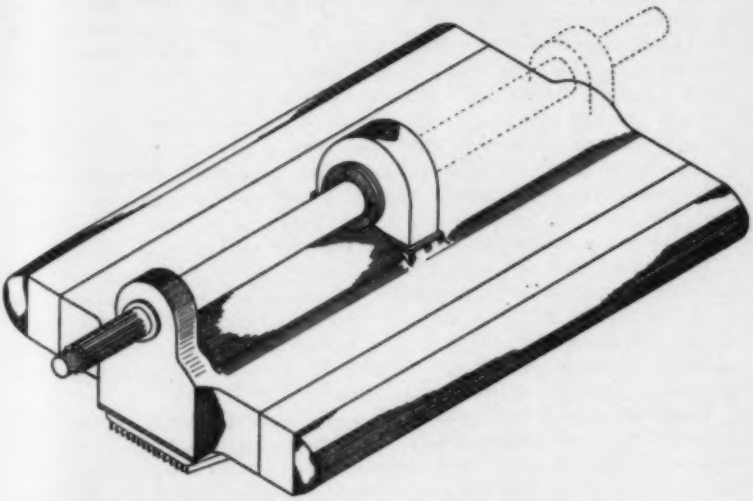

FIG. 10.

FLAT ENGINE FOR POWERS OF 1500 TO 2000 B.H.P., APPROXIMATELY 35–40 LITRES SWEPT VOLUME.

engine and the number of cylinders employed, but will be between, say, 35 and 45 litres.

As to the form which such engines will take; the *X* engine, with four banks of six cylinders, each arranged at 90° to the other, around a single crankshaft, is a promising method of obtaining powers as high as 2000 b.h.p. from one unit; or an engine of narrow X form, with two banks of six cylinders at 60° or less, opposed to two similar banks.

For a lower power, about 1500 b.h.p., or for an exceedingly high duty and compact engine, the scheme shown in Fig. 10 is one which I put forward for consideration, because it is intended to allow for more than the usual number of cylinders in-line, and avoid those difficulties attendant on the use of a long crankshaft.

The engine is of the flat type, with two banks of six or more horizontally

opposed cylinders. The crankshaft consists of two sections with the main airscrew reduction drive pinion and, possibly, the camshaft and accessory drive pinions, bolted in between them.

The engine is designed for mounting inside the wing or at the leading edge. Referring to the illustration in Fig. 10, it will be appreciated that it is a relatively simple matter to arrange a double airscrew drive, one tractor and one pusher, or a single remote drive either for tractor or pusher purposes. Such an engine should be designed with low stroke/bore ratio, and have a normal maximum speed between 3000 and 3500 r.p.m. With a total capacity of 36–40 litres, 1600–1800 b.h.p. might be expected.

As a matter of interest and to show what can be done by using specially prepared fuels, I have reproduced, in Figs. 11, 12 and 13, some performance curves of the Rolls-Royce "R" engine, which was so successful in the Schneider Contest of 1931. The "R" engine had a cylinder capacity of 36·6 litres (2240 cu. in.) and ran at a normal speed of 3200 r.p.m. The operating b.m.e.p. was between 260 and 270 lb. per sq. in.

I am greatly indebted to Messrs. Rolls-Royce Limited and the Air Ministry for permission to publish this data.

The curves in Fig. 11 show the difference in power on the same engine (1931) obtained with two fuels. One fuel was that originally made up for the 1929 Schneider Contest, and it was used as a reference fuel, against which to compare new fuel blends for the 1931 engine.

The original fuel, as the reference, was composed of 22 per cent. aviation gasoline, 78 per cent. benzole, plus 4 ml. of lead per Imperial gallon. The final fuel, for the 1931 Contest, was designed to give better operating conditions, compared with the fuel for the successful 1929 engine; and consisted of 20 per cent. aviation gasoline, 70 per cent. benzole, 10 per cent. methanol, plus 4 ml. of lead per Imperial gallon.

It will be noted that the 1931 fuel gave a lower specific fuel consumption than the reference (1929), despite the former's lower calorific value. The reason for this was that it was necessary, with the 1929 fuel, to run rather rich in order to cool the engine; whereas the 1931 fuel allowed the engine to run cooler, and it could then be adjusted to give the normal consumption commensurate with the heat value of the fuel.

In Fig. 12, two power curves are shown, one giving the engine performance with the fuel prepared for the Contest (20/70/10 + 4), and the other shows the performance with a special fuel consisting of 30 per cent. benzole, 60 per cent. methanol, 10 per cent. acetone plus 5 ml. of lead per gallon. The latter fuel was particularly designed for the World's Speed Record, and was responsible for an increase in power, from the same engine, of about 200 b.h.p. This was the first occasion on which the Speed Record was raised above 400 m.p.h.

The curves in Fig. 13 show the effect of the increase of latent heat of the fuel upon power, boost temperature and pressure.

In connection with this work it is interesting to note that, whereas the "R" engine gave a phenomenal power output with these fuels, it was water-cooled. But only recently was the 20/70/10 fuel tried in a high-duty liquid-cooled engine having high-temperature cooling, and violent pre-ignition occurred which caused serious damage to the engine.

This, and the examples given previously in the paper, serve to show that

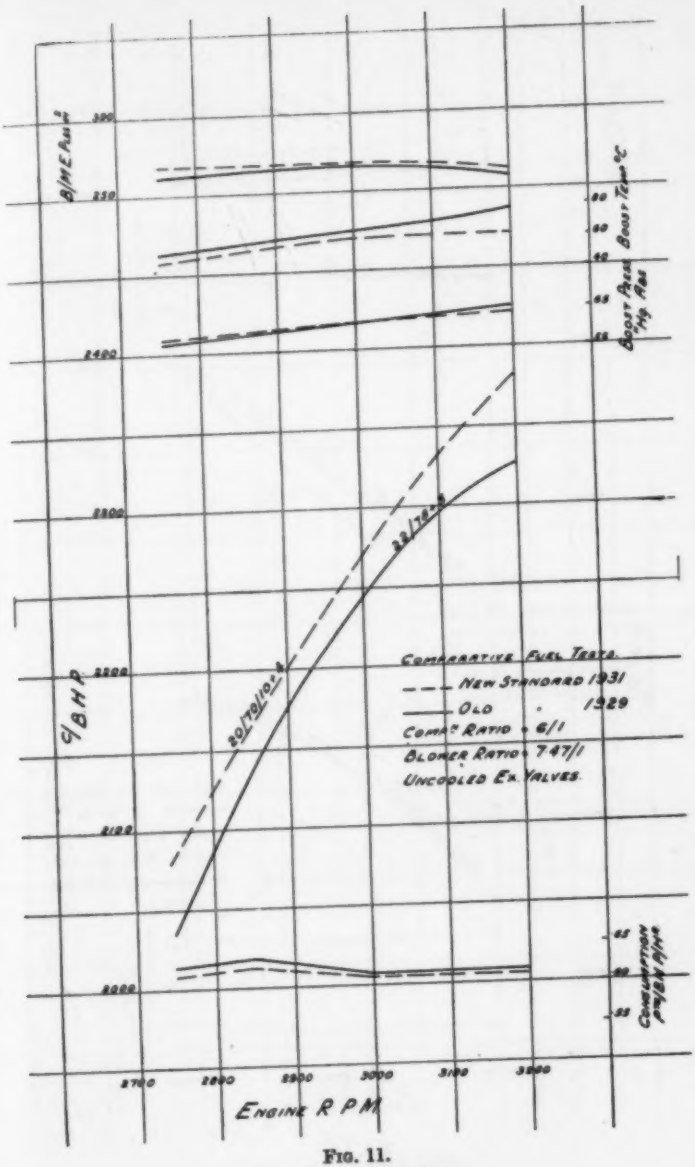


Fig. 11.

R.R. "R" Engine 1931.

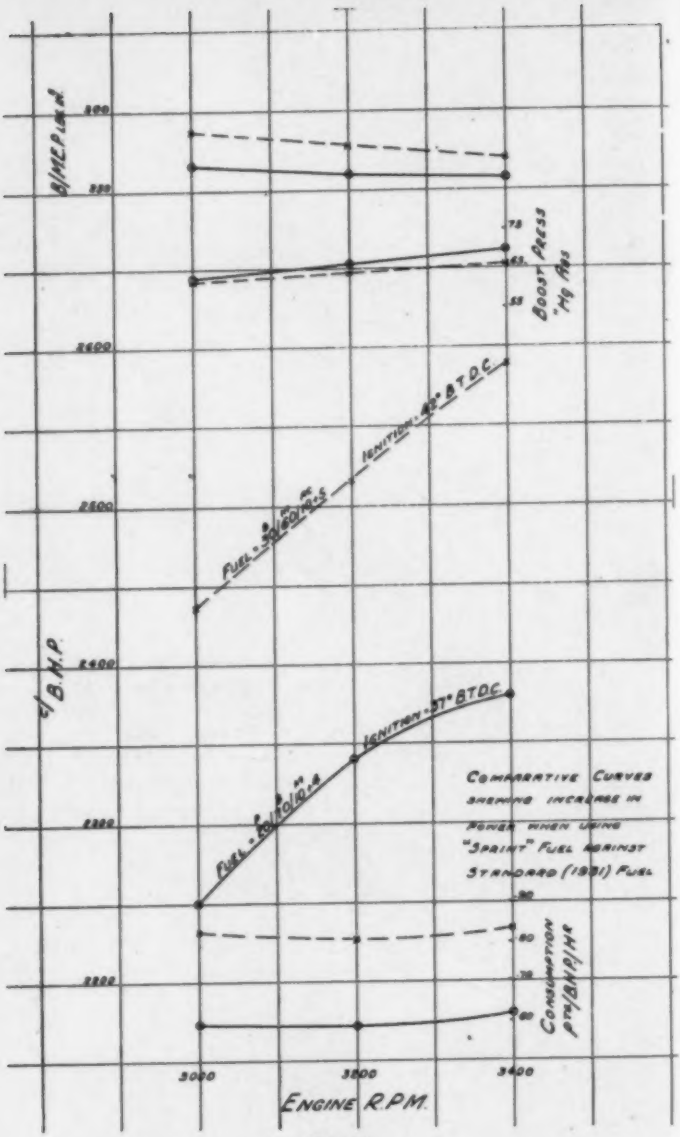


FIG. 12.
R.R. "R" ENGINE 1931.

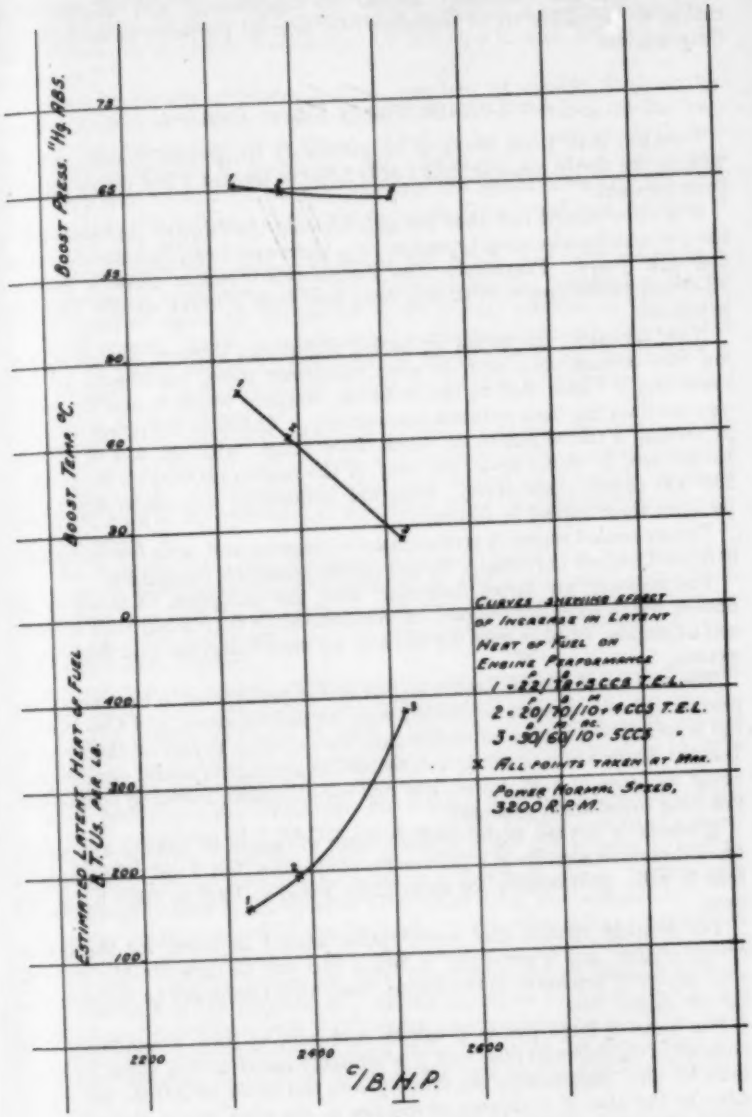
Boost Press. "Hg abs.
Boost Temp. °C.
Estimated Latent Heat of Fuel C.T.U.s per lb.
C/B.H.P.
Curves showing effect of increase in latent heat of fuel on engine performance
1 - 22/70/10 + 4 CCS T.E.L.
2 - 20/70/10 + 4 CCS T.E.L.
3 - 30/60/10 + 5 CCS "
X All points taken at max. power normal speed, 3200 R.P.M.

FIG. 13.

R.R. "R" ENGINE 1931.

alcohol fuels are extremely critical to temperature and therefore are rather too unstable to be considered for normal purposes in modern high duty engines.

## Air Cooling versus Liquid Cooling.

I realize that I am treading on extremely dangerous ground, even by writing the above heading, but I only hope to present a few points for your consideration.

It is an accepted fact that the gap between the relative performances of the air- and liquid-cooled types has been narrowed down considerably in the last few years. Previously, the liquid-cooled engine gave a superior all-round performance, with less drag and with a lower specific fuel consumption.

Now, however, the radial air-cooled engine can show an almost equally low fuel consumption and, in some particular cases, has shown an even lower one.[14] Also, due to the N.A.C.A. cowling, which is now in general use, the drag has been reduced considerably. Although the power absorbed in cooling a radial engine of about 1000 b.h.p., with the aid of cylinder baffles, etc., is about 10–15 per cent. of the maximum output, at speeds of 200–300 m.p.h. respectively, there are indications that these figures will be more than halved in future.

The air-cooled engine is predominant in America and, with few exceptions, it is used almost universally by the airline-operating companies.

The military air forces, however, with the exception of those in the States, which have only about one representative type fitted with a liquid-cooled engine, employ both liquid- and air-cooled engines to a fairly equal extent.

The success of the air-cooled engine is due principally to the energy and resourcefulness of those concerned with its development, and also because the liquid-cooled engine manufacturers were content to rest on their laurels. But the latter are now doing a considerable amount of sound development along the lines of high power, low fuel consumption, low drag cooling and low drag installation generally.

Whether or not the liquid-cooled engine will again be used to any extent for commercial aircraft is a matter for conjecture, but I am of the opinion that it will; particularly for large units, rated at 1500 to 2000 b.h.p. and over.

The average specific fuel consumption should be lower for the liquid-cooled engine, and it generally is, but it can still be considerably reduced, with probably less harm to the engine, than would normally be the case with the air-cooled job.

For units of large power it will be necessary to have a relatively large number of cylinders in line, and it is probably easier to cool these by liquid than by air; particularly for b.m.e.p.'s in the order of 200 lb. per sq. in. Also, in the case of a number of engines in the wing, the radiators can be arranged remote from the engines and in the best possible positions to suit aerodynamic requirements; whereas it is not going to be easy to arrange for efficient cooling of large air-cooled engines similarly placed.

With the new technique of induced flow and fitting radiators in ducts,

or tunnels, engines can be cooled for very small expenditure in drag. About 2·5–3·5 per cent. of their maximum power is all that is needed for a high-temperature liquid-cooled installation at 200 m.p.h. and 300 m.p.h., respectively.[11]

It must be clearly understood, when speaking of cooling drag, or the power absorbed to cool the engine, that this has little bearing on the form drag of the installation as a whole. That is to say, although it may eventually be possible to reduce the drag, necessary to cool a radial, to a figure very close to that for an in-line engine, the frontal area and the form of the engine will still be a dominant factor so far as it affects the drag of the aircraft as a whole.

For exceedingly high speeds, of about 300 m.p.h. and over, assuming a given power in both cases, the liquid-cooled engine installation should give a superior speed of around 30 or 40 m.p.h., relative to the radial air-cooled motor: which is considerable when one considers the probable increase in power necessary for such an improvement in speed with a given aircraft. The liquid-cooled engine should then be a more economical proposition in this sphere.

Personally, I think that there is a place for both types, and certainly the air-cooled engine should hold its own up to and including a rated power of about 1500 b.h.p. Although air cooling may be used for powers in excess of this figure, I am of the opinion that it will then be more satisfactory to employ liquid cooling.

At the moment there does not seem to be any limit to the capabilities of both types in the matter of power production, and it will mainly depend on the manner in which the power from either unit (air or liquid) can best be utilized, all other things, such as fuel consumption, installed weight, etc., being reasonably similar.

Amongst the air-cooled protagonists a controversy still rages as to whether single- or double-row radial engines are desirable.

For rated powers in excess of 1000 b.h.p. it is probable that it will be necessary to use the double-row radial, but it is contended that up to 1000 b.h.p. the single-row radial can do the job.

This is probably a fair statement, but I think that the single-row engine with large cylinders, of a similar total capacity to the two-row, will be more fuel sensitive than the latter or, conversely, will require a fuel of higher octane number for the same total output in both cases; particularly when take-off powers in the order of 1100–1200 b.h.p. are considered.

That the single-row radial can be made to run with equal smoothness of a twin-row of similar power has been practically proved in the case of the "Cyclone" engine, having the loose balance weight, or floating kidney, on the rear web of the crankshaft. Airline operators in the United States informed me that this engine was a great improvement on anything that they had previously experienced, and it had reduced or eliminated air-screw hub "scuffing" and, also, the wear and tear on the whole installation was less.

The twin-row radial has, however, some inherent advantages which make it very attractive for the present types of high-speed civil and military aircraft. It has a smaller overall diameter than the single-row engine, for a given cylinder capacity, and is probably less fuel sensitive because of its

smaller cylinders. Also, it can be run at higher speeds, and will probably give a higher power output than a similar single-row motor.

It is said that the twin-row radial does not have an advantage proportional to its smaller diameter because, for a given cylinder capacity, it requires more air to cool it, due to the addition of another row of cylinders and the heating of the air as it passes from the front to the rear row. Also, the cowling will have a greater chord, which is important in the case of high-speed machines, since any increase in the wetted surface means a considerable percentage increase in drag.

## Miscellaneous.

I have not, so far, mentioned the carburettor icing problem, because it scarcely comes within the scope of this paper. But I consider it to be of such importance that I have referred to four important papers on the subject.[17] The Chandler-Groves carburettor, mentioned by the authors of two of the papers ("Ice" by S. Paul Johnston and "Aircraft Engine Design and Operating Problems" by Arthur Nutt), appears to be a very promising development in the prevention of carburettor icing, and avoids pre-heating the inlet air.

A further interesting development is shown in Fig. 14. This carburettor has been produced by the Zenith Carburetter Company, Limited, and has the jets located above the throttle and between it and the engine. Although it is not yet in general use, this instrument shows great promise, and is a valuable contribution in solving the icing problem.

According to Nutt, and others, the present method of treating the icing problem is to pre-heat the inlet air to the carburettor, so that the temperature of the fuel/air mixture issuing from the carburettor is not less than 35° F. This means that the inlet air has to be heated to about 100° F.

Nutt (in the same paper) disagrees with the idea of allowing the pilot to overload the engine by means of the boost "over-ride" regulator, which device is often fitted in conjunction with the automatic boost control; and he is undoubtedly correct in his objections, because the greatest risk of damage to the engine is incurred at take-off conditions.

With regard to the testing of sparking-plugs prior to their acceptance, the engine firms are often far too casual in their methods of testing new plug types. Generally, the plug is handed over to one of the experimental test staff, who fits it to any unit which happens to be available at the moment, and then proceeds to "knock the stuffing out of it," afterwards handing it back to the plug manufacturer without any advice as to how it could be improved, beyond a bare statement to the effect that it failed to stand up to the test; which in all probability was not at all representative of operating conditions in a full-scale engine.

All plugs should be submitted to a carefully controlled test, the procedure of which involves running them in a high-duty single-cylinder unit, and making a series of mixture "loops" with increasing boost, until a point is reached where failure occurs or pre-ignition sets in. Only in this manner can plugs be correctly classified and rated according to their capabilities, and the effect of any modifications in design noted. You are referred again

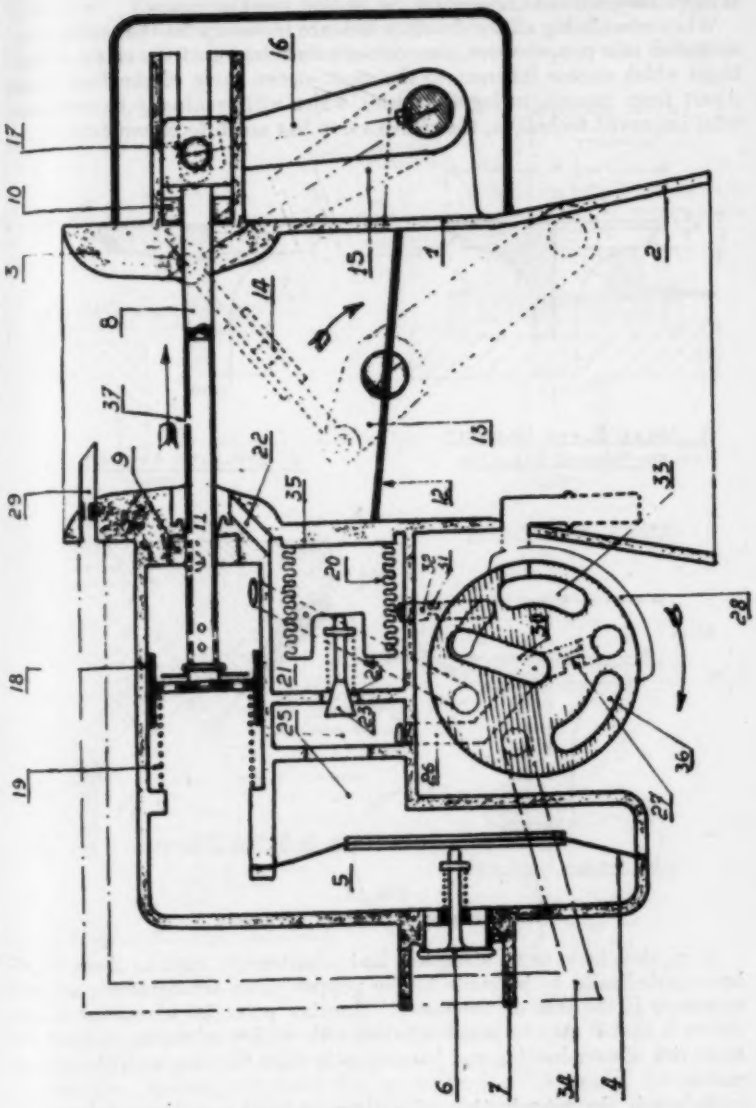
16
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FIG. 14.

to Nutt's paper, in which is given, in detail, the method adopted by the Wright Aeronautical Corporation for testing sparking-plugs.

When considering all the details which are necessary for the satisfactory operation of a poppet valve, one cannot help thinking of the many advantages which appear inherent to the single-sleeve valve of the Burt type. Apart from manufacturing difficulties, which will eventually be overcome with improved technique, the sleeve valve has much to recommend it.

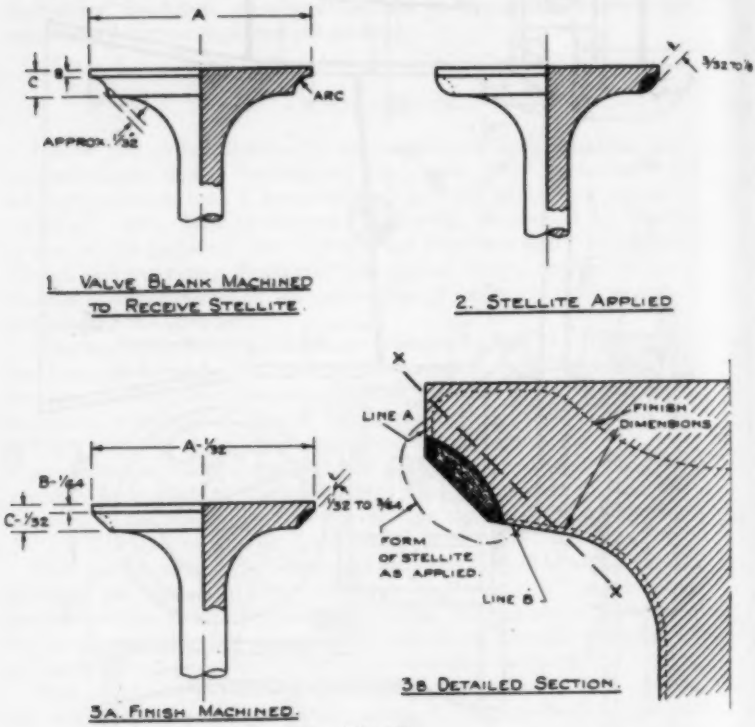


FIG. 15.

SEQUENCE OF STELLITING OPERATION.

It requires little or no attention, and adjustments, such as those which have periodically to be made to the poppet valve arrangement, are not necessary in the case of the sleeve. Another potential advantage of the sleeve is that it may be possible to run with weaker mixtures, without the same risk of over-heating and burning as is often the case with the poppet valve.

Although the introduction of sodium cooling, continuous lubrication and automatic tappet adjustment has largely overcome the principal disadvantages of the latter, particularly so far as the air-cooled engine is concerned, periodical checks must still be made; whereas the sleeve valve

will operate without attention until a complete overhaul of the engine is necessary. Even then there should be little to do, and the sleeve proper may even last the whole life of the engine.

The elimination of valve springs, cam gear, rocker arms, etc., is a great

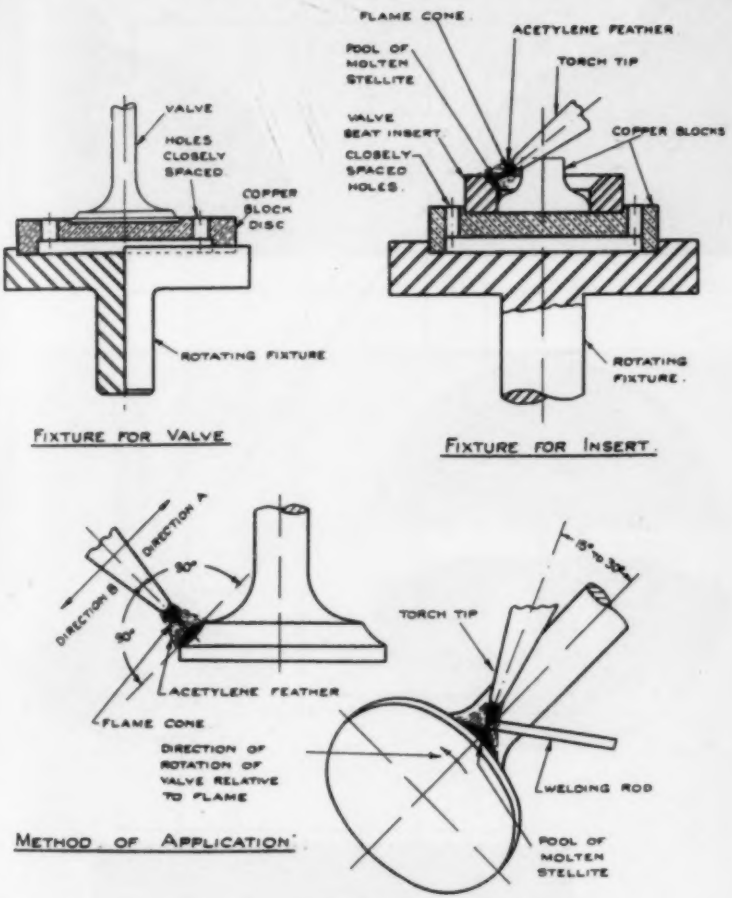


FIG. 16.

DETAILS OF STELLITING OPERATION.

advantage. Accuracy of valve timing, which is so important for efficient engine operation over long periods, is practically inherent to the sleeve valve, and there is little "lost motion" to account for, as is the case with the other arrangement. The sleeve valve is also mechanically silent.

Perhaps the single sleeve may eventually supersede the poppet valve,

and it will almost certainly be employed on level terms with the latter, in the case of new engine types, during the next three to five years.

I do not wish to infer that the poppet-valve arrangement is dead, technically. Actually, its production does not, at the moment, present so

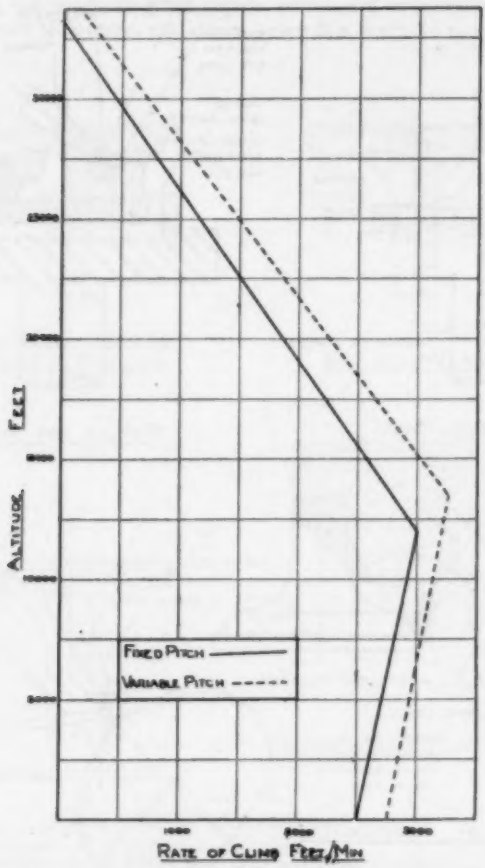


FIG. 10.

RATE OF CLIMB CURVE FOR A MODERN FIGHTER.

much difficulty as that of the sleeve, and it is also quite efficient both from the point of view of mechanical and volumetric efficiency.

Beyond mentioning that the exhaust valve of the modern engine is stellited, I have not said anything about the method of applying Stellite, because this has already been dealt with fairly fully in my previous paper.[7] However, I have reproduced, in Figs. 15 and 16, the stelliting procedure in

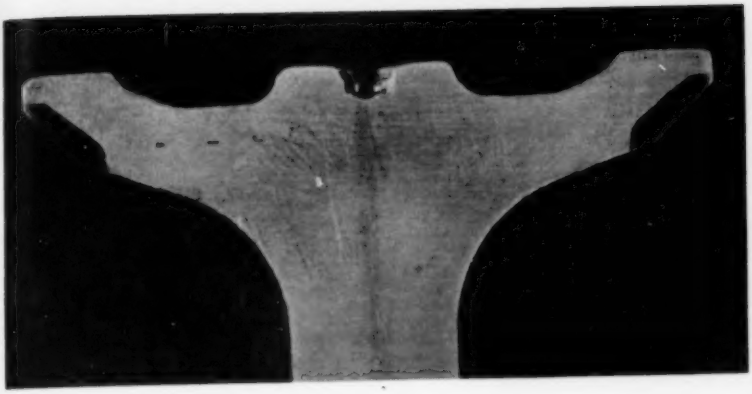

FIG. 17.

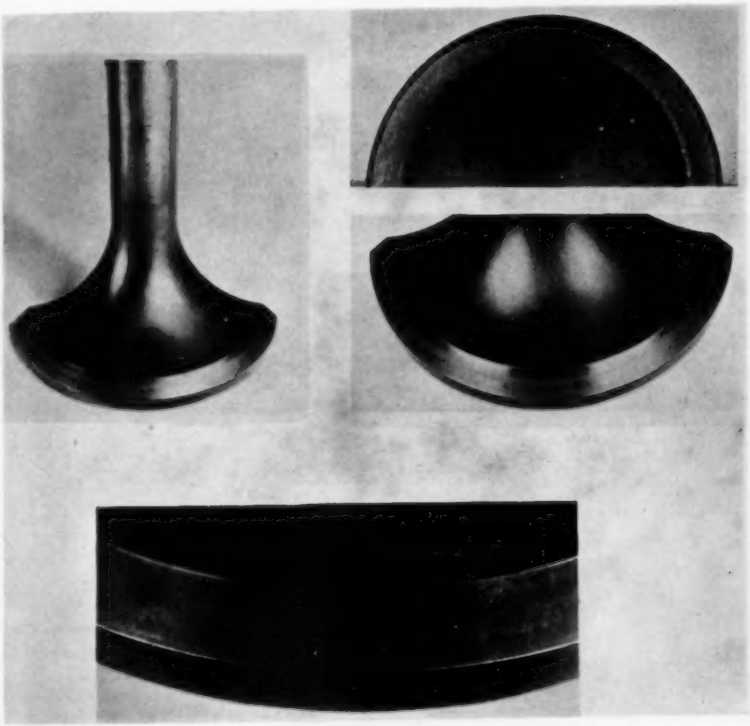

FIG. 18.

[*To face p.* 118.

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pictorial form, and this may be helpful to those of you who are interested from the production aspect.

Fig. 17 shows a sectioned and stellited valve, to which the Stellite has been applied in a special type of groove cut in the valve seat. This particular

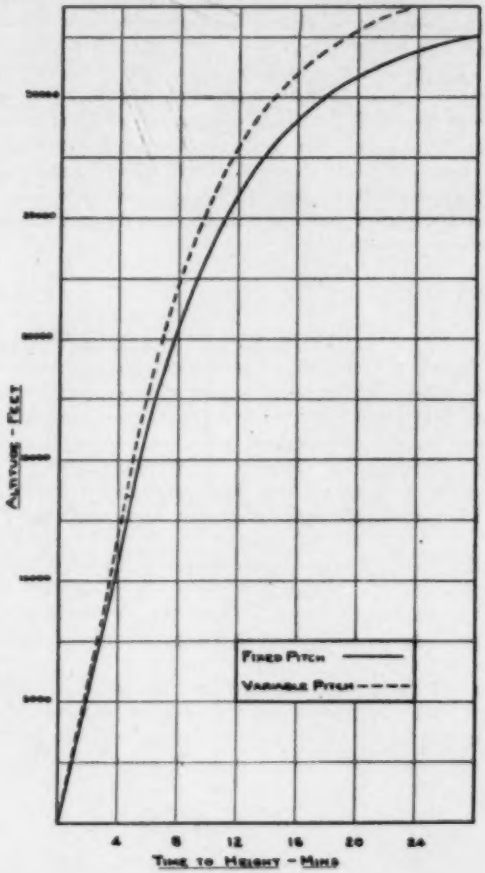


FIG. 20.

TIME TO HEIGHT CURVE FOR A MODERN FIGHTER.

method assists the operator by giving him some datum line to work to, and also ensures that a similar amount of Stellite, per valve, is used.

Fig. 18 gives four views of a sodium-filled and stellited valve, which has operated in an engine, for periods totalling over 2000 hours, without trouble and with a fuel having a lead concentration of about 3 ml. per Imperial gallon. This shows what can be done by the proper application of modern technique.

In connection with the cleaning of exhaust valves which, after running for some time on leaded fuel, collect a hard and adherent deposit on their heads, seats and necks; I have reproduced, in Appendix III, a very satisfactory method of cleaning them, which has been developed by the Ethyl Gasoline Laboratories, Detroit. This is an electrolytic method, and the removal of the deposit can be effected without etching the valve steel, which is a very important feature.

Finally, in Figs. 19 and 20, are given the "rate of climb" and "time to height" curves of a fast modern single-seat fighter; first, with a fixed-pitch airscrew and, secondly (dotted), with a two-position controllable pitch screw. These curves give some idea of what can be done at present with a fuel of 87 octane (modified Motor Method), which is now in general use, and suggest that, with 100 octane fuel and a constant-speed airscrew, a high-speed heavily loaded machine will be capable of a maximum rate of climb of more than 4000 ft. per minute.

## Conclusion.

In conclusion, I hope that I have provided sufficient practical information, enabling you to obtain some idea of the difficulties encountered by the aero engine manufacturers in the development of their engines; and, also, a glimpse of the efforts which are being made by the oil companies, in order to assist the aero engine to progress.

We have only touched the fringe, so far as the synthesis of fuels is concerned, and many more fuels or blending agents will probably be discovered in future, which may be equal to, or better than, *iso*octane or di*iso*propyl to ether.

Assuming that there is little possibility of producing a material, or fuel, which will not detonate at all, or cause pre-ignition, any new blending agents found in the future should be sensitive to additions of tetraethyl lead, otherwise their potentialities will tend to be considerably reduced and employment restricted.

In this paper, I have purposely excluded all reference to the subject of lubrication. This is obviously a problem of great importance in connection with the use of the higher-octane-number fuels, but it is definitely outside the scope of my paper, and I feel that there are others more competent to deal with the question.

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[11] "Liquid-Cooled Aero Engines," by H. Wood, *J.S.A.E.*, July 1936.
[12] "Engine Types and Requirements for Preparation of Fuels," by F. C. Mock, *J.S.A.E.*, July 1936.
[13] "Future Possibilities of 100-Octane Aircraft Engine Fuel," by Lt. F. D. Klein, *J.S.A.E.*, August 1936.
[14] "Radial Aircraft Engine Performance Possibilities," by Raymond W. Young, *J.S.A.E.*, June 1936.
[15] "Mixture Strength in Petrol Engines Continuously Controlled by Electric Exhaust Gas Analysers," by Boerlage and Peletier, *Journal of the Royal Aeronautical Society*, November 1936.
[16] "Possible Future Developments of Air-Cooled Aero Engines," by A. H. R. Fedden, *Journal of the Royal Aeronautical Society*, March 1934.
[17] "Ice Formation in Carburetters," by W. C. Clothier, *Proceedings of the Royal Aeronautical Society*, February 1935.
"Ice Formation in Aircraft Engine Carburetters," by H. H. Allen, G. C. Rodgers, and D. C. Brookes, *J.S.A.E.*, November 1934.
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## APPENDIX I

### AIRCRAFT ENGINE PERFORMANCE WITH 100 OCTANE FUEL.*

By F. D. KLEIN, *Air Corps, Wright Field.*

*(Presented at the Power Plants and Fuels Session, Third Annual Meeting, I.Ae.S.)*

#### INTRODUCTION.

WITH the present use of Air Corps Specification No. Y–3557–G fuel having an anti-knock value of 92 octane by the method of test covered in Air Corps specification No. 3566, in engines designed for maximum performance on such fuel, an increase of about 33⅓ per cent. in power output per unit weight has been obtained over that possible with earlier type engines which operated with about 50 octane number fuel prior to 1928. Until recently, anti-knock value higher than the present Air Corps standard did not appear to be practicable for service use because of prohibitive cost, limited availability and necessarily high lead content resulting in excessive corrosion difficulties.

Developments of the fuel industry made possible early in 1934 the production of commercial *iso*octane on a large scale at a cost sufficiently low to make the outlook for higher anti-knock fuels appear decidedly promising. The Air Corps, anticipating a need for 100 octane fuel, prepared an experimental specification, No. X–3575, for such fuel on February 1, 1934. This specification has now been distributed to leading fuel refiners for comments preliminary to adoption of the fuel as standard. In addition to increase in anti-knock value, the maximum allowable lead content has been reduced in this specification to 3 ml. per gallon, as compared with the 6 ml. per gallon allowed in Air Corps specification No. Y–3557–G. Fuel furnished on current procurement to specification Y–3557–G has in general contained from 3·5 to 5·5 ml. of lead per gallon, averaging about 4·0 ml. An adequate potential supply of 100 octane fuel appears to be available with a lead content of close to, but not greater than 3·0 ml. per gallon. Thus, the higher anti-knock value will be accompanied by a reduction in engine corrosion.

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* Reprinted by courtesy of the Institute of the Aeronautical Sciences, U.S.A., from *J.Ae.S.*, Vol. 2, March 1935.

One thousand gallons of commercial *iso*octane (2 : 2 : 4-trimethylpentane) was procured in May 1934 to be blended with good quality aviation gasoline to make 2000 gallons of 100 octane fuel containing 3·0 ml. of tetraethyl lead per gallon, sufficient for experimental multi-cylinder engine tests to determine the increase in power output possible with such fuel.

### Description of Tests.

As a result of considerable preliminary determinations of physical properties and anti-knock value of various fuels available, four were selected as being of the greatest interest for comparison with 92 octane specification Y–3557–G fuel in multi-cylinder aircraft engines. Each of these four fuels had an anti-knock value of 100 octane by the Air Corps method of test, and each conformed closely with all other requirements of specification X–3575 except in tetraethyl lead content. A brief description of the four fuels is given in Table I.

Table I.

| Power Plant Fuel No. | Composition of Base Fuel. | $PbEt_4$ per Gal. |
|---|---|---|
| 530 | 50% *iso*octane + 50% aviation gasoline . . . . | 3·0 ml. |
| 531 | 50% *iso*octane + 50% aviation gasoline . . . . | 6·0 ,, |
| 532 | Standard Reference Fuel C-6 . . . . . | 8·5 ,, |
| 533 | 37·5% *iso*octane + 37·5% high anti-knock fuel about half composed of aromatics + 25% *iso*pentane . . . | 1·0 ,, |

Fuel No. 531 differed from Fuel No. 530 only in lead content, as shown, and was included in the tests to determine whether any increase in power output would be obtained due to the additional lead, the knock tests showing no appreciable difference in anti-knock value apparently due to the poor lead susceptibility of 100 octane fuels. In fuel No. 533, the *iso*octane was used to increase the anti-knock value and lead susceptibility of the aromatic fuel, and the *iso*pentane was added to reduce the A.S.T.M. 10 per cent. evaporated point so that it would conform to the requirements of specification X–3575.

A brief description of the two engines used is given in Table II.

Table II.

| Commercial Name. | Compression Ratio. | Impeller Gear Ratio. | Impeller Diameter. | R.P.M. used during Tests. |
|---|---|---|---|---|
| Wasp . . . . | 6 : 1 | 14 : 1 | 6½ in. | 2200 |
| Cyclone . . . | 6·4 : 1 | 10 : 1 | 11 ,, | 1950 |

The following tests were conducted with the Wasp engine :—

(1) Constant throttle mixture control runs with each of the four 100 octane fuels and the Y–3557–G fuel.

(2) Constant specific fuel consumption, variable throttle runs with each of these five fuels at specific fuel consumption of approximately 0·55 lb. per brake horse-power per hour.

(3) Constant specific fuel consumption, variable throttle runs with Fuels Nos. 530 and 531 and specification Y–3557–G fuel, at specific fuel consumptions of approximately 0·62 and 0·72 lb. per brake horse-power per hour.

On these variable throttle runs, the throttle was opened progressively until the maximum allowable cylinder temperature of 550° F. was reached.

With the "Cyclone" engine, constant specific fuel consumption, variable throttle runs were made with each of the five fuels. A reduced air blast was used so that detonation more quickly would be indicated by increase in cylinder temperature.

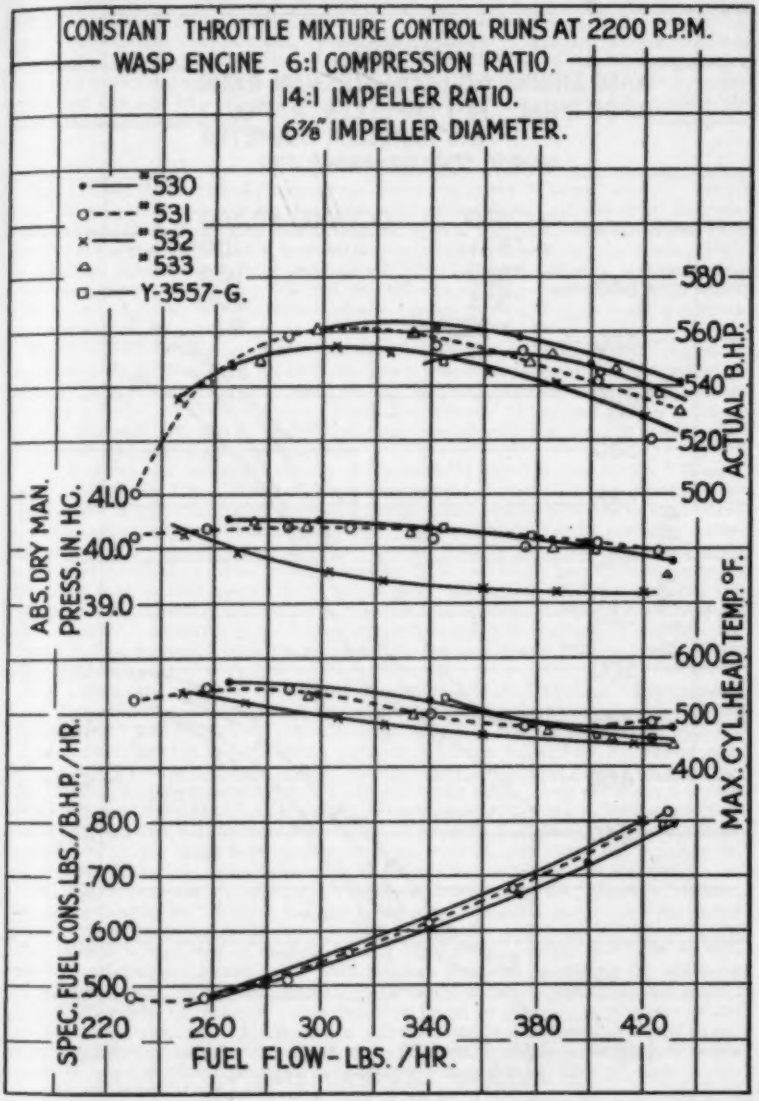
CONSTANT THROTTLE MIXTURE CONTROL RUNS AT 2200 R.P.M.
WASP ENGINE. 6:1 COMPRESSION RATIO.
14:1 IMPELLER RATIO.
6⅞" IMPELLER DIAMETER.
"530
"531
"532
"533
Y-3557-G.
ABS. DRY MAN. PRESS. IN. HG.
41.0
40.0
39.0
ACTUAL B.H.P.
580
560
540
520
500
MAX. CYL. HEAD TEMP. °F.
600
500
400
SPEC. FUEL CONS. LBS./B.H.P./HR.
.800
.700
.600
.500
220
260
300
340
380
420
FUEL FLOW - LBS./HR.

FIG. 1.

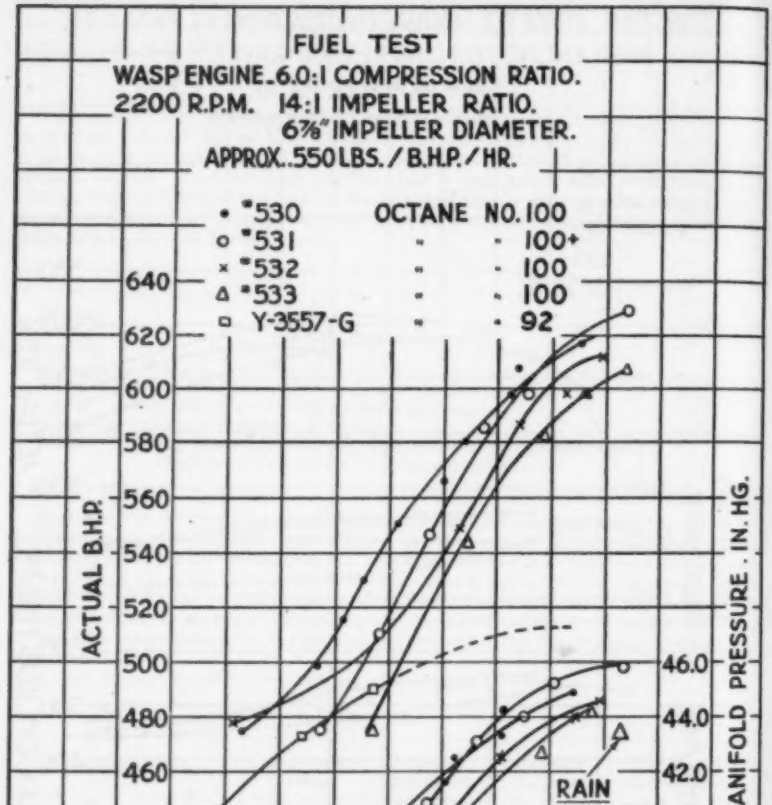
FUEL TEST
WASP ENGINE. 6.0:1 COMPRESSION RATIO.
2200 R.P.M. 14:1 IMPELLER RATIO.
6⅞" IMPELLER DIAMETER.
APPROX. 550 LBS. / B.H.P. / HR.
• *530 OCTANE NO. 100
o *531 " 100+
× *532 " 100
△ *533 " 100
□ Y-3557-G " 92
ACTUAL B.H.P.
640
620
600
580
560
540
520
500
480
460
440
ABSOLUTE DRY MANIFOLD PRESSURE . IN. HG.
46.0
44.0
42.0
40.0
38.0
36.0
34.0
RAIN
440
460
480
500
520
540
AVERAGE CYL. HEAD TEMP. °F.

FIG. 2.

Runs were made at specific fuel consumptions of approximately 0·60 and 0·80 lb. per brake horse-power per hour. The throttle was opened progressively in each case until the engine suddenly became very rough and cut out. This occurred before excessive cylinder temperatures were reached. The exhausts indicated detonation just before cutting out occurred, but no rapid increase in cylinder temperature was apparent except in the case of the specification Y–3557–G fuel, with which it appeared that excessive temperature would soon be reached. It is possible that the irregular operation was due to preignition or to failure of the spark plugs to fire consistently under the high compression pressure existing.

### Results.

Fig. 1 shows the results of the mixture control run in the "Wasp" engine. Actual brake horse-power, absolute dry manifold pressure, maximum cylinder head temperature and specific fuel consumption are plotted against fuel flow. The curves for Fuel No. 532 are apparently in error, as there is no satisfactory explanation for the variation in manifold pressure, and later tests showed little difference between this and other 100 octane fuels. Neglecting this fuel, the other three 100 octane fuels appear equal, and the specification Y–3557–G fuel appears inferior in view of the excessive cylinder temperature experienced.

Fig. 2 shows the results of the variable throttle run in the "Wasp" engine at approximately 0·55 lb. per brake horse-power per hour specific fuel consumption. Actual brake horse-power and absolute dry manifold pressure are plotted against average cylinder head temperature. Fuels Nos. 530 and 531 appear slightly superior to Nos. 532 and 533, and show 620 h.p. as compared with 510 h.p. for specification Y–3557–G fuel, a 21·6 per cent. increase.

Fig. 3 shows the composite results of the variable throttle runs in the "Wasp" engine with Fuels Nos. 530 and 531 and specification Y–3557–G fuel. Actual brake horse-power is plotted against average cylinder head temperature. The solid curve was obtained at a specific fuel consumption of approximately 0·55 lb. per brake horse-power per hour; the dotted curve approximately 0·62 lb. per brake horse-power per hour; and the broken curve approximately 0·72 lb. per brake horse-power per hour. It is seen that at 0·62 specific fuel consumption, 650 h.p. is obtained with the 100 octane fuel as compared with 540 h.p. with the specification Y–3557–G fuel, a 20 per cent. increase. At 0·72 specific fuel consumption, 650 h.p. is obtained with the 100 octane fuel as compared with 580 h.p. with the specification Y–3557–G fuel, a 12 per cent. increase.

Fig. 4 shows the results of the variable throttle run in the "Cyclone" engine, using all of the five fuels. Actual brake horse-power is plotted against average cylinder head temperature. The solid curve was obtained at a specific fuel consumption of approximately 0·60 lb. per brake horse-power per hour. In this engine Fuel No. 533 appears to be about 2 octane numbers poorer than the other 100 octane fuels. At a specific fuel consumption of approximately 0·60 lb. per brake horse-power per hour, it is seen that Fuels Nos. 530 and 531 show 800 h.p., as compared with 610 h.p. for the specification Y–3557–G fuel, a 31 per cent. increase. At a specific fuel consumption of approximately 0·80 lb. per brake horse-power per hour, Fuel No. 530 shows 830 h.p. as compared with 670 h.p. for the specification Y–3557–G fuel, a 24 per cent. increase.

The greater increase in power output obtained in the case of the "Cyclone" engine, as compared with the "Wasp," was due to the special impeller used to give extremely high degree of supercharge, in order to show, as clearly as possible at this time, the value of 100 octane fuel in engines having high enough output available to take sufficient advantage of such fuel. With engines designed specifically for operation on 100 octane fuel, still greater gain in performance should be obtained, particularly at high altitudes. Anti-knock value has been found to decrease at the rate of one octane number per 11–18° F. increase in mixture temperature, as that highly-supercharged engines, to take full advantage of the high anti-knock value of the fuel, would probably require intercoolers for maximum performance on take-off and at low altitude, regardless of the anti-knock value of the fuel used.

The multi-cylinder engine tests show close agreement of the 100 octane fuels with their rating in the C.F.R. engine under the Air Corps method of test, with the one exception of Fuel No. 533 which in the "Cyclone" engine appears to be about two octane numbers lower than indicated by the C.F.R. knock test. It is interesting to



ABSOLUTE DRY MANIFOLD PRESSURE . IN. HG.

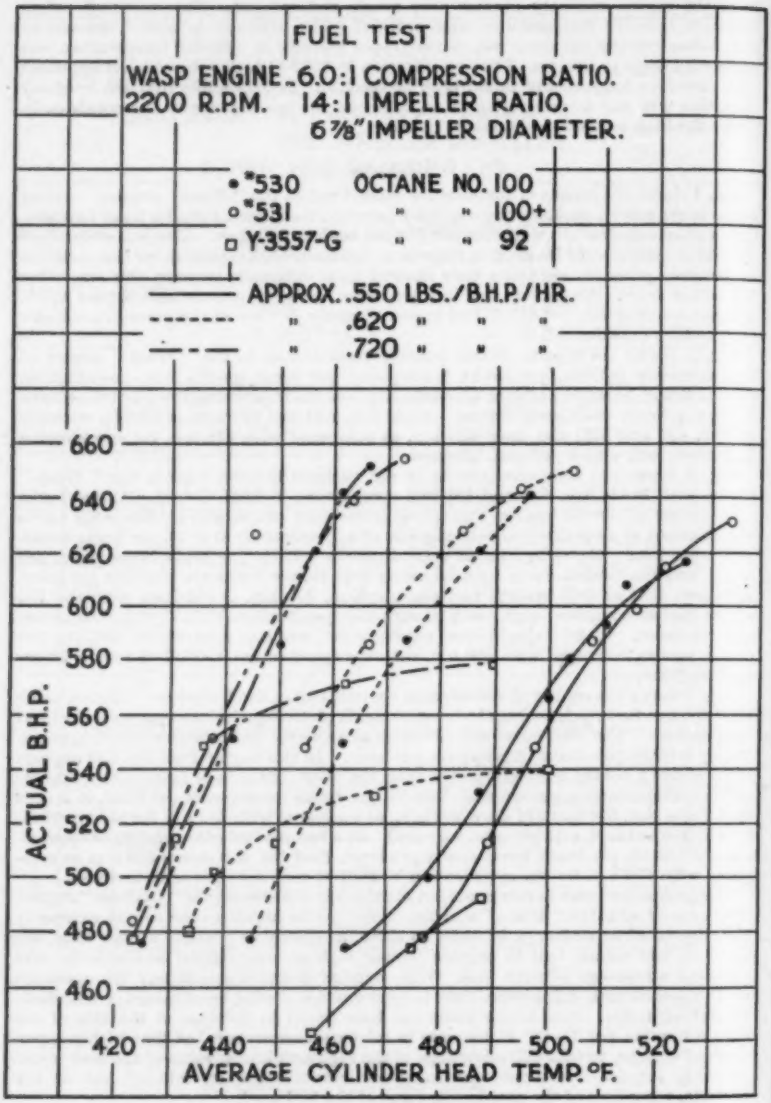
FUEL TEST
WASP ENGINE..6.0:1 COMPRESSION RATIO.
2200 R.P.M. 14:1 IMPELLER RATIO.
6⅞" IMPELLER DIAMETER.
•*530 OCTANE NO. 100
○*531 " " 100+
□ Y-3557-G " " 92
APPROX..550 LBS./B.H.P./HR.
" .620 " " "
" .720 " " "
ACTUAL B.H.P.
660
640
620
600
580
560
540
520
500
480
460
420
440
460
480
500
520
AVERAGE CYLINDER HEAD TEMP. °F.

FIG. 3.

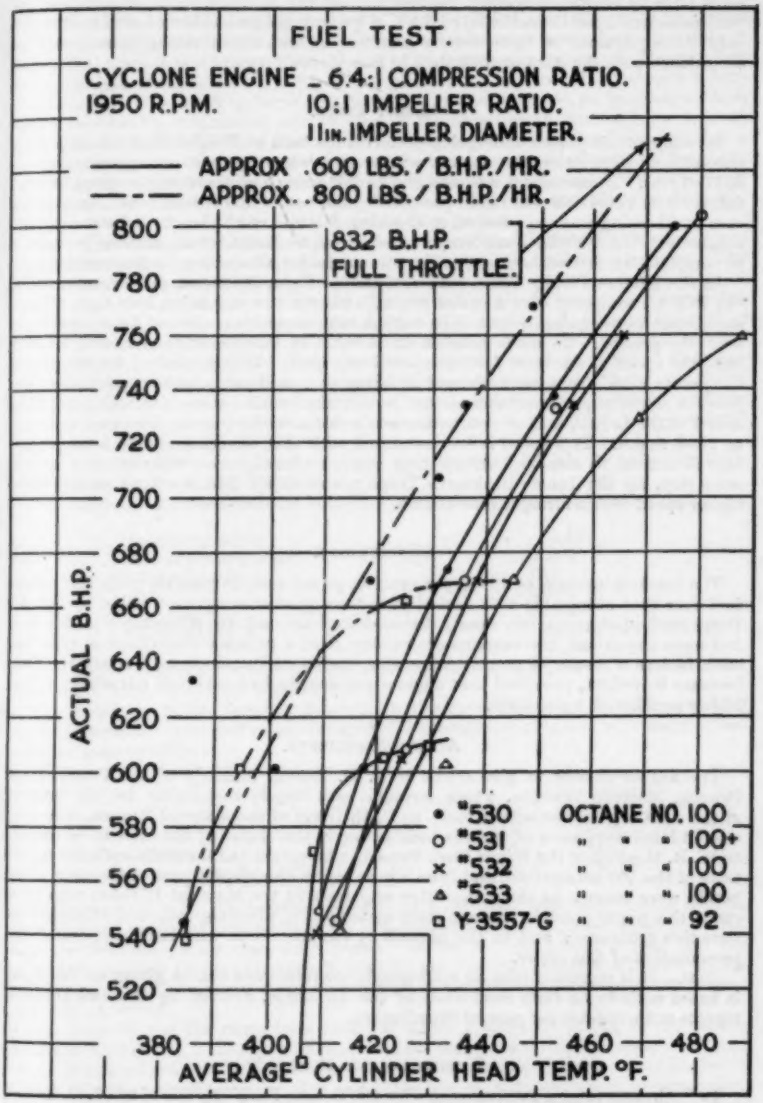
FUEL TEST.
CYCLONE ENGINE _ 6.4:1 COMPRESSION RATIO.
1950 R.P.M. 10:1 IMPELLER RATIO.
11in. IMPELLER DIAMETER.
APPROX .600 LBS. / B.H.P./HR.
APPROX. .800 LBS. / B.H.P./HR.
832 B.H.P.
FULL THROTTLE.
ACTUAL B.H.P.
800
780
760
740
720
700
680
660
640
620
600
580
560
540
520
380
400
420
440
460
480
AVERAGE CYLINDER HEAD TEMP. °F.
"530 OCTANE NO. 100
"531 " " " 100+
"532 " " " 100
"533 " " " 100
Y-3557-G " " " 92

FIG. 4.

note that Fuel No. 531, although it contains more lead than Fuel No. 530, is rated the same both by the multi-cylinder engines and the C.F.R. engine. In this connection, pure *iso*octane upon the addition of 3 ml. of lead per gallon has been found to increase only the equivalent of three octane numbers in anti-knock value, when tested in accordance with the Air Corps method of knock test.

### Flight Tests.

Several pursuit planes undergoing performance tests at Wright Field recently have encountered difficulties, the engines overheating when operated on specification Y–3557–G fuel. In one case it was essential to determine high speed on the speed course; full throttle operation was made possible by the use of 100 octane fuel. In another case overheating was experienced in checking the rate of climb; by substituting 100 octane fuel, the cylinder head temperatures dropped about 30° C., making it possible to complete the test without exceeding the maximum allowable cylinder temperature.

In the Mitchel Trophy Race, held at Selfridge Field, Michigan, in November 1934, ten P-26A's competed over a closed five-mile course, the race being four laps. These aeroplanes were equipped with high-output engines which could not be opened fully near the ground. To make possible an increase in the power output, and thereby raise the speed of the race, 100 octane fuel was used. This permitted the aeroplanes to operate with a reasonable margin of safety at considerably higher speed than was possible on the original performance test on a straight course at sea level using specification Y–3557–G fuel, and no detonation was evident to the pilots. The race was won at 216·8 m.p.h. This speed is low compared with that of racing planes, because this race is limited to standard service type pursuit planes. In a different race on the same day, for the Junior Birdmen's Trophy, a similar P-26A averaged considerably higher speed over a straight mile course.

### Conclusions.

The marked increase of 15–30 per cent. in power output possible with 100 octane fuel over that obtainable with fuel of 92 octane number anti-knock value by the Air Corps method of knock test clearly demonstrated not only the advantages of this fuel, but more important, the extreme desirability from a military standpoint of adopting such fuel as a means of greatly increasing engine performance with relatively little increase in weight, provided that engines are designed to take full advantage of the higher anti-knock value fuels.

### Acknowledgments.

The author desires to give credit to S. D. Heron, formerly of the Power Plant Branch, Material Division, whose foresight was largely responsible for the interest of the Air Corps in 100 octane fuel; to E. R. Irwin of the Material Branch, who conducted laboratory tests of various fuels aiding in the choice of the fuels to be tested; to W. R. Hopkins of the Power Plant Branch, who conducted the multi-cylinder engine tests of the 100 octane fuel, and from whose report the greater part of the data given herein were taken; to the many other engineers of the Material Division who have made this paper possible through their assistance in planning tests and offering constructive criticisms; and to the officials of the Air Corps who have authorized the presentation of this paper.

*Note.*—It is regretted that no bibliography or references can be given, as the paper is based entirely on tests conducted by the Air Corps, covered by Material Division reports not available for general distribution.

### Letter to the Editor.*

In "Aircraft Engine Performance with 100 Octane Fuel," by one of us (F. D. Klein), and published in your March 1935 issue, it is stated that the response of pure *iso*octane to additions of tetraethyl lead is low. It is further stated that an addition of 3 c.c.

* Reprinted by courtesy of the Institute of the Aeronautical Sciences, U.S.A., from *J.Ae.S.*, Vol. 2, May 1935.

of tetraethyl lead per U.S. gal. to *iso*octane only results in a gain equivalent to three octane numbers when tested in accordance with Air Corps specification 3566.

In the discussion following the paper Dr. Edgar pointed out that the three octane number gain obtained from 3 c.c. of lead might actually represent a very large gain in fuel value, since it was known that the size of an octane number rapidly increased at the upper end of the scale. Dr. Edgar also pointed out that even if successive octane numbers were of sensibly uniform size at the 100 end of the scale, an increase of three might represent a substantial gain in view of the increases in performance reported for 8 octane numbers between 92 and 100. It was also stated in the discussion that a test programme was in progress to determine the lead response of commercial *iso*octane in a full-scale supercharged engine. This work has now been carried out as a result of co-operation between the Lycoming Manufacturing Co., the Material Division, U.S. Army Air Corps, and the Ethyl Gasoline Corporation.

The engine tests were carried out by the Lycoming Manufacturing Co. using a supercharged aircraft engine cylinder of normal type having high wall temperatures. The intake air at the point where it entered the induction system had a temperature of 203° F., and this in conjunction with the cylinder wall temperatures attained subjected the fuels tested to extremely severe conditions. The method of test involved raising the air pressure at the entrance to the induction system until the maximum possible power output for each fuel tested was reached. At each boost pressure on each fuel tested, specific fuel consumption and spark advance were adjusted to the conditions giving maximum power. Three fuels were tested as follows: (*a*) leaded aviation gasoline meeting the requirements of Air Corps specification Y–3557–G, (*b*) commercial *iso*octane and (*c*) commercial *iso*octane plus 3 c.c. of tetraethyl lead per U.S. gal.

The aviation gasoline used had an octane number of 92 by Air Corps specification 3566 and 87 by the C.F.R. Motor Method.

The commercial octane had the following physical and chemical characteristics:

| | |
|---|---|
| Specific Gravity | 0·692 |
| Initial Boiling Point | 210·4° F. |
| 90% recovered | 210·7 |
| 96% „ | 211·1 |
| End point | 217·4 |
| Unsaturated | 3% or less |

The clear commercial octane had an octane number of 99½ by A.C. specification 3566 and 99½ by the C.F.R. Motor Method.

The maximum power outputs, reached for the three fuels, and the corresponding manifold pressure expressed as percentages of the maximum obtained with the aviation gasoline were as follows:

| | Power. | Absolute manifold pressure. |
|---|---|---|
| Y–3557–G | 100% | 100% |
| *iso*Octane | 117% | 114% |
| „ plus 3 c.c. $PbEt_4$ | 134% | 128% |

In the case of both the aviation gasoline and the clear *iso*octane violent audible knock was occurring at maximum power and further increase of boost pressure caused a power decrease rather than an increase. In the test of *iso*octane plus lead the maximum possible power output as limited by the fuel was not reached since, at the capacity limit of the supercharger, no evidence of audible knock or any other distress could be observed.

The behaviour of the three fuels tested is shown graphically in Fig 1. In all the points plotted in Fig. 1 the spark advance was 35° except in the case of clear *iso*octane, where it was retarded to 30° at the highest manifold pressure on account of excessive knock. In the case of *iso*octane plus lead at the highest manifold pressure obtainable, spark settings of both 25° and 40° were tested. Since the available manifold pressure would not cause signs of distress, increase of spark advance was tried as a means of producing fuel breakdown, but resulted in no change of engine performance.

As evidence that the lead response of octane was not determined under abnormally favourable conditions it may be mentioned that the indicated specific fuel consumption

was 0·425 lb. per h.p.-hr, at the maximum output developed on *iso*octane plus 3 c.c. of lead.

It is clear from these data that lead in *iso*octane is highly effective in increasing engine performance whatever the lead response in terms of octane numbers as measured by conventional knock-testing methods may be.

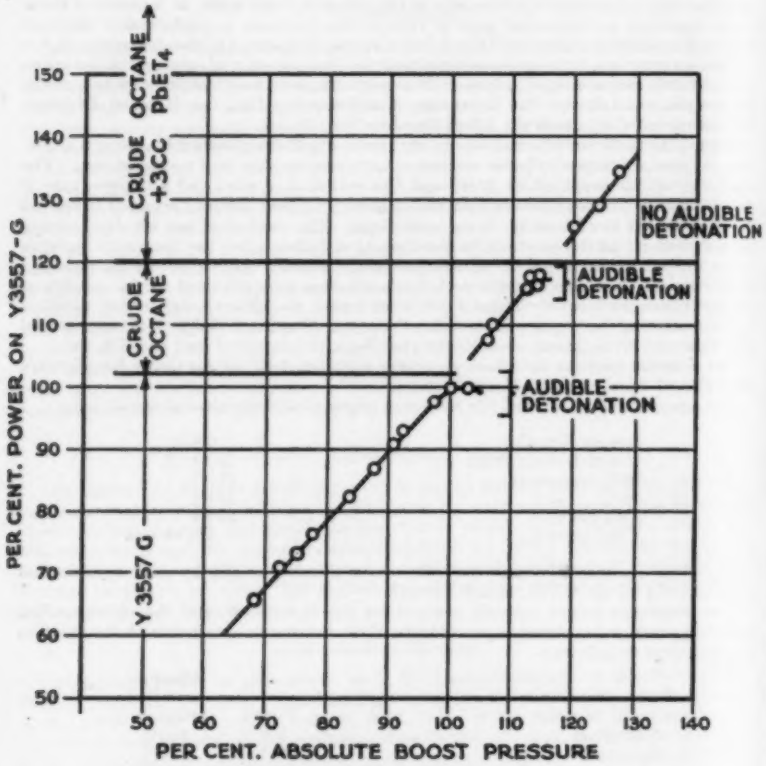


FIG. 1.

The data also indicate that *iso*octane plus tetraethyl lead can be used to advantage with very high mixture temperatures. It is stated in the above-mentioned paper that intercoolers are desirable for use with 100 octane fuel and highly supercharged engines. While there is no question of the correctness of this conclusion, nevertheless it does appear that, although supercharger intercoolers are desirable, they are not essential to obtain considerable advantage from fuels of 100 octane number or over.

VAL. CRONSTEDT.
R. N. DUBOIS.
F. D. KLEIN.
S. D. HERON.

*April* 24, 1935.

# APPENDIX II.

## DIRECTIONS FOR MANUFACTURING

## *E.G.* 174.*

### I. Introduction.

E.G. 174 is a compound of lard oil, triethanolamine, butanol and aluminium stearate. The first three are liquids, the latter a light powder. The formula is:

| | |
|---|---|
| Triethanolamine | 5–6% by weight |
| Normal butanol | 10–12% " |
| Aluminium stearate | 10% " |
| Lard oil | Balance |

For the important specifications of these materials see Section II. The general procedure of manufacture is to heat together all the materials except the butanol, which has a relatively low boiling point, and to add the butanol when the hot homogeneous mixture of the other components has become cool enough. In making the mixture homogeneous it is important to grind the aluminium stearate thoroughly into the oil, and for this reason if it is made on a large scale (above 5 gallon lots) efficient mechanical equipment must be available. It must allow of heating the contents up to 110° C.

### II. Raw Material Specifications.

#### 1. *Lard Oil.*

The lard boil must be fairly closely controlled as to acidity. The acidity required, calculated as oleic, is between 3½ and 7½ per cent. The importance of observing these limits lies in securing the proper excess of the base triethanolamine over the fatty acid. An excess between 2 and 4 per cent. is given by the acid limits mentioned above.

For manufacturing purposes, to secure uniformity of product it is better to start always with a uniform acidity, say 6 per cent. In many cases, the oil supplier is in a position to supply oil of specified acidity. In other cases the maker of E.G. 174 may, if desired, adjust the content of the oil by adding No. 2 oil to increase the acidity of Prime Burning oil to reduce it, the acid contents of the various oils being determined by titration.

#### 2. *Triethanolamine.*

Commercial triethanolamine with a combining weight of about 132 and a water content of not more than 1·5 per cent. is used.

#### 3. *N-Butanol.*

The *n*-butanol used should be essentially water-free.

#### 4. *Aluminium Stearate.*

Aluminium stearate is found on the market with widely varying content of impurities and moisture. At present experience has not been sufficient to allow the framing of specifications for this material. Batches both high and low in sulphate and with varying aluminium content have been used with equal success. Even the removal of water has not been found to have much influence, although it can be said that on general principles the water content ought to be as low as possible. The possibility of obtaining an improved aluminium stearate will be discussed in Section V.

### III. Raw Material Analysis.

#### 1. *Lard Oil.*

*Determination of Acidity.*—For the determination of the acidity of lard oil the solutions required are:

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* Reprinted from Ethyl Gasoline Corpn. Rpt., No. C.R.17.

Potassium hydroxide solution, about 0·1 normal.
Alcohol (any alcohol miscible with water).
Phenolphthalein solution, 0·1% in alcohol.

Place 10 c.c. of the oil in a flask with a stopper, add 50 c.c. of alcohol and 1 to 2 c.c. of phenolphthalein solution, then titrate with the KOH solution. When the contents of the flask remain pink after vigorous shaking for 1 minute, the oil has been neutralized.

The acidity of the oil expressed as per cent. by weight of oleic acid is calculated as follows:

(c.c. KOH) × (normality of KOH solution) × (2·82) = per cent. oleic acid by weight.

*N.B.*—If the alcohol used is acid, it should be neutralized before use, or a blank determination should be made.

2. *Triethanolamine.*

A 5-gram sample should be diluted to 200 c.c. with water, 2 drops of a 0·1 per cent. solution of methyl orange then added, and the solution titrated with normal hydrochloric acid to the first change in colour.

3. *Aluminium Stearate.*

(*a*) *Moisture.*—Moisture may be determined by placing a sample in a drying oven at a temperature not higher than 105° C. until constant weight is attained.

(*b*) *Sulphates.*—Sulphates may be determined by grinding a sample of the stearate with hot water, filtering and precipitating sulphate in the filtrate as barium sulphate by adding barium chloride. The results may be in error owing to the difficulty of wetting the stearate powder.

A more exact method for sulphates is the following: Place a sample of aluminium stearate in intimate mixture with 3 times its weight of Eschka's mixture (1 anhydrous sodium carbonate + 2 magnesium oxide) in a crucible, and cover the mixture with an equal amount of Eschka's mixture. Heat in a muffle furnace, starting cold and raising to full heat in several hours, to drive off the carbon. Then treat with hot water, filter and determine the sulphate in the filtrate as barium sulphate by adding barium chloride.

(*c*) *Aluminium.*—Aluminium may be determined by the following method. Place a weighed sample (1–2 gram) of the stearate in a beaker and heat to fuming with 10 c.c. sulphuric acid S.G. 1·8 to char the organic part of the soap.* Then add nitric acid (S.G. 1·4) dropwise to the hot mixture until the organic matter is completely destroyed, i.e., a colourless solution is obtained.† Dilute to 150 c.c. with water, neutralize, add ammonium chloride and precipitate aluminium as hydroxide by adding ammonia. Filter the precipitate and ignite filter paper and precipitate in a weighed crucible, weighing as aluminium oxide, $Al_2O_3$.

4. *E.G.* 174 *for Aluminium, Triethanolamine and Fatty Acid.*

(*a*) *Aluminium.*—Aluminium in the finished product may be determined by burning a 15–20-gram sample and finally igniting in a muffle, the white ash being assumed to be aluminium oxide $Al_2O_3$.

(*b*) *Triethanolamine, Fatty Acid.*—The total amount of triethanolamine in a sample may be determined by titration with normal acid. The result includes both the free base and that in the form of soap. Similarly the total amount of fatty acid may be obtained by titrating with *N*/10 alkali. A comparison of the acid and base equivalents thus found will indicate the amount of free triethanolamine in the sample.

## IV. Directions for Manufacturing.

These directions should be followed:—

Place the whole of the aluminium stearate in a mixer equipped for scraping or grinding, as well as agitation, and add the whole of the triethanolamine and about half

* If the mixture goes solid, add 1–2 c.c. additional sulphuric acid to make fluid.

† Two large crystals of anhydrous ammonium sulphate may be added to the hot sulphuric solution after oxidation to free it of all nitric oxides before dilution.

the lard oil. Stir these materials together until a heavy cream free from lumps is obtained. The remainder of the lard oil may then be added and heat applied. On reaching a temperature of about 100° C. the fluid will become clear and brown. The temperature should never be allowed to exceed 120° C., and should not be kept above 100° any longer than is necessary. When a clear homogeneous liquid has been obtained, the mixture may be allowed to cool with or without stirring, and when the temperature has reached 60° C. the butanol should be added with stirring. Cooling is continued, and between 50° and 40° C. the liquid should be pumped into storage tanks through a filter to remove inorganic impurities and foreign matter. It is important not to filter cold. If the hot filtration is omitted, the same result may be obtained by settling, and decanting the clear material from the top of the storage tanks. The latter is in any case desirable because of the occasional appearance of insoluble sludge or mud which slowly settles to the bottom of the storage tank.

## V. General Remarks.

(*a*) *Viscosity of Product.*—The viscosity of E.G. 174 is approximately 550 sec. S.U.V. at 100° F.

Variation in the content of butanol and of aluminium stearate can cause variations in viscosity. Thus a mixture containing 8 per cent. of aluminium stearate and 12 per cent. butanol has a viscosity of about 350 sec. Replacing the aluminium stearate entirely by lard oil results in a viscosity of about 150 secs. which has been found to be too low for efficient protection against corrosion.

(*b*) *Stability of Product.*—The use of aluminium stearate introduces some problems due to occasional instability of the mixture. Under some conditions of manufacture the liquid product sometimes becomes almost filled with a cream-coloured semi-solid precipitation which settles extremely slowly. The volume of the material thus separating is deceiving, since ultimately it settles until occupying less than 5 per cent. of the original liquid volume. It is a soft jelly, making a suspension with the lard oil which does not allow of filtration. There is some evidence that violent mechanical agitation or filtration of the mixture *while cold* encourages the precipitation of this new phase, and it has been observed that if filtration is carried out at as high a temperature as is feasible—50–60° C.—such a precipitation is usually avoided.

Occasionally the precipitation occurs in a rather different form, in which a liquid phase separates in amount 5–7 per cent. of the whole, while the more usual solid precipitation may be present or almost entirely absent. It is believed that this separation can be largely prevented by a slight increase in the amount of butanol.

In any case, allowing the product to stand for as long as possible, preferably at least two weeks, then decanting the upper portion, gives a product free from any sediment and of satisfactory stability.

(*c*) *Chemical Nature of the Aluminium Soap.*—Some of the problems of stability encountered in the preparation of E.G. 174 find their basis in the chemical nature of aluminium stearate. The purified aluminium stearate of commerce has an aluminium content between 3·2 and 4·8, corresponding to compositions between monosterate 4·5 per cent. and distearate 3·1 per cent. The presence of sulphate in the samples indicates that some of them at least are made by double decomposition between sodium stearate and aluminium sulphate. The soap made by this method can be altered in composition by extraction with such mild solvents as ether and acetone, which extract 1 mol. of stearic acid for each 2 atoms of aluminium present. Alcohol, on the other hand, extracts 2 mols. stearic acid per 2 atoms of aluminium. These results show that the chemical nature of aluminium stearate is not simple. It appears likely that hot lard oil may also be able to liberate stearic acid from the soap, and that the solid precipitation sometimes obtained in the product may have resulted in this way by the formation, for instance, of triethanolamine stearate with the free base present. From these considerations it would appear that extracted aluminium stearate would have more desirable properties for E.G. 174 than the commercial soap, but up to the present it has not been found possible to obtain the modified product in suitable amounts to test this question.

The occasional formation of a second liquid layer presumably results from a condition of near saturation of some of the components of the complicated mixture, which may occasionally pass saturation. There is little doubt that this can be corrected,

when it occurs, by addition of a little extra butanol or other solvent, although mere decantation of the upper layer would be suitable in most cases.

A spray apparatus for spraying cylinders with high-viscosity oils as protectives has been developed by the DeVilbiss Company.

The maker's description and instructions for use of this apparatus are as follows:

"This unit consists of a 2-gallon pressure tank to supply the protective oil and a C.L.F. type spray gun with an extension nozzle, bent so as to reach all the interior surfaces of the cylinder, together with a 15-ft. length of air hose and a 15-ft. length of fluid hose for connecting the gun to the tank.

"The spray gun has an aluminium body with a pistol grip handle and a two-finger trigger for opening the air and fluid valves. The extension nozzle on the spray gun is $\frac{3}{8}$ in. diameter, and bent so as to enter the cylinder through the spark plug-hole and spray all of the interior surfaces evenly. This extension has an outer steel tube, through which the air passes, and an inner flexible metal tube, through which the fluid passes. The nozzle is designed to give a conical spray. The outer tube can be turned to any desired position by loosening the large knurled nut that holds it to the gun body. This will make it easier to spray all the cylinders without unnecessary manipulation of the spray gun. If it is desired to take the extension apart, it is necessary to remove the small slotted tip at the nozzle first, then remove the nut holding the outer tube to the gun body. The outer tube can then be pulled off of the inner flexible tubing. The nozzle parts are made of alloy steel, heat treated, and will not be damaged by hard usage.

"The tank is of a 2 gallon capacity, 6 in. in diameter, and 18 in. long; the shell is $\frac{3}{32}$ in. thick and the heads are $\frac{1}{8}$ in. thick, of welded construction. The tank is tested to 350 lb. hydrostatic pressure after welding. A handle is welded on the side of the tank with which to carry it. If desired, a sling can be made to carry the tank from the shoulder or on the back of the operator. The tank is equipped with an air inlet connection of the quick detachable type; one part is left on the tank and one part, with $\frac{1}{4}$ in. female pipe thread, is left on the air-supply hose. This part has a valve built in it that closes automatically when the connection is detached. The connection is attached by means of the bayonet lock. The incoming air branches off at the tee on the tank so as to supply both the tank and gun. The air hose, which is red, is connected to the tee on the tank, and the end with the bent connection is connected to the threaded boss on the side of the gun body. The valve near the side of the tank head is the fluid outlet valve, and the black hose is connected to this and the threaded boss on the bottom of the gun body. This hose has a special oil-resisting liner to prevent swelling and softening. A fluid tube is soldered on the fluid outlet valve, and runs nearly to the bottom of the tank, so that practically all of the fluid can be removed. Also on the tank head is a wing screw plug which is a combination filler plug and relief valve. Backing this plug out three or four turns allows the air in the tank to escape through two vent holes in the filler plug.

"A handy feature on this unit is the ability to blow all the oil in the fluid hose and gun back into the tank in case it is desired to disconnect the hose or when the work is finished. This is done as follows: Close the air inlet valve on the tank, open the relief holes at the filler plug on the tank, have the fluid valve on the tank open, then close the circular slot at the nozzle of the gun by wrapping the fingers around it, or in some other way, and pull the trigger on the gun all the way back. The air then blows the oil back through the gun and hose into the tank. By listening to the tank, the air can be heard bubbling through the oil when the gun and hose are empty. It is not necessary to do this if the tank is emptied by spraying.

"Air pressure to tank and gun should be set at about 50 lb. In coating the interior of the cylinders, the gun extension is inserted through the spark-plug hole until the nozzle is as close as possible to the piston crown surface. The trigger on the gun is then pulled and the extension withdrawn. The gun should be moved so that the spray nozzle moves in the largest possible circle as it is being withdrawn."

The complete spray apparatus and a close-up of the gun are shown in Figs. A and B. The gun is shown in two positions in a Pratt and Whitney Wasp cylinder in Figs. C and D. The spray apparatus shown in Fig. A is an excellent device for the rapid treatment of cylinders, and was specifically developed to spray high viscosity oils

FIG. A.

[*To face p.* 134.

Fig. B.

Fig. C.

FIG. D.

which spray with difficulty when an approximately conical spray discharge is required. With 50 lb. air pressure the apparatus sprays 150 c.c. of E.G. 174 in about 20 sec. The cost of this gun is about $70.00 in small lots.

## APPENDIX III

### THE ELECTROLYTIC CLEANING OF EXHAUST VALVES.*

By S. D. Heron, George Calingaert and F. J. Dykstra

(*Research Laboratories, Ethyl Gasoline Corp.*)

It is often desired to remove completely the deposits, such as engine carbon, scale and lead compounds, and the like, which are found on exhaust valves, without removing any of the underlying metal. Similarly, in the case of scaling test-specimens, forgings, and so on, it is often desired to clean the surface down to the metal before inspection.

An article † by U. C. Tainton, entitled "A New Process for the Cleaning of Metals," applies particularly to the de-scaling of wire prior to drawing operations. This process consists in using the metal to be cleaned as the cathode in a bath of fused sodium hydroxide–sodium carbonate. The applicability of this method to the cleaning of exhaust valves was investigated, and, after several variations had been tried out, a procedure was finally adopted which appears to be practical and efficient. The equipment and method used in this laboratory are described here.

#### Procedure.

(*A*) *Description of the Equipment.*—The necessary equipment comprises essentially a heated electrolytic bath, a 6-volt storage-battery, suitable leads with clamps and an ammeter. The set-up used in this laboratory for the cleaning of valves is illustrated in Fig. 1. A switch has been added which permits reversal of the current, as will be explained. Additional equipment comprises a Transite shield to prevent spattering when the valve is lowered into the electrolyte, a stirring rod, metal prongs, a brass-wire brush, and a "spacer." The latter is a section of 3-in. steel-tubing $\frac{1}{2}$ in. shorter than the depth of the bath. On account of the danger of handling molten alkali, it is important to provide a laboratory coat with sleeves, canvas gloves with gauntlets, and goggles.

(*B*) *Preparation of the Bath.*—The electrolyte is first prepared by putting into the melting pot 600 grams of caustic soda and 200 grams of sodium carbonate. With the lid on the pot, this mixture is heated until it is melted. Traces of moisture in the materials may cause the melt to froth at first. If this occurs, the heating process is slowed down until the frothing subsides. When the level of the material is lowered by melting, an additional 200 grams of sodium carbonate is added in one or more portions and the process repeated. The composition of the melt is thus 60 : 40 caustic soda–sodium carbonate. Appreciable deviations from these proportions have little if any effect on the cleaning process.

(*C*) *Preparation of the Valve.*—Any excess of oily material which might react violently with the molten alkali is first removed from the valve, either by heating in a flame or by washing with kerosene or gasoline. The spacer serves to set the depth of immersion of the valve so that it comes approximately $\frac{1}{2}$ in. from the bottom of the pot. This is done by standing the valve in the middle of the spacer, slipping the transite shield over the stem until it rests on the spacer, and fastening the spring-clamp connection flush against the shield.

(*D*) *The Cleaning Process.*—When the bath is up to temperature, which is indicated by the fact that the melt is fluid and no longer froths or boils, the lid is removed. The operator holds the valve by the tip of the stem by means of the prongs, and lowers the valve and shield assembly on to the bath. The shield practically covers the bath before the valve touches the melt, thereby minimizing the danger of spattering.

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* Reprinted by courtesy of the Society of Automotive Engineers, U.S.A., from *J.S.A.E.*, Dec. 1935.

† See *Wire and Wire Products*, Vol. 9, 1934, p. 399.

The resistance of the system is preferably adjusted so that the ammeter indicates approximately a 6-amp. discharge with valves from 1¼ to 3 in. in diameter. Depending on the thickness of the deposit, and also on the shape of the valve, the electrolysis is continued for 2 to 5 min. The valve assembly is then removed from the bath, this time by grasping the edge of the shield instead of the valve stem. This assembly is removed, the lead and shield are removed and the valve is immersed in water. After the solidified caustic has been dissolved off, the remaining thin film is brushed off by means of the brass-wire brush.

The valve should now have a clean metallic appearance. If the deposit has not been completely removed, particularly in some inaccessible places, the operation may be repeated.

NOTES.

(1) Technical grade caustic soda may be used, in powder, flakes or any other convenient form. The sodium carbonate should be anhydrous.

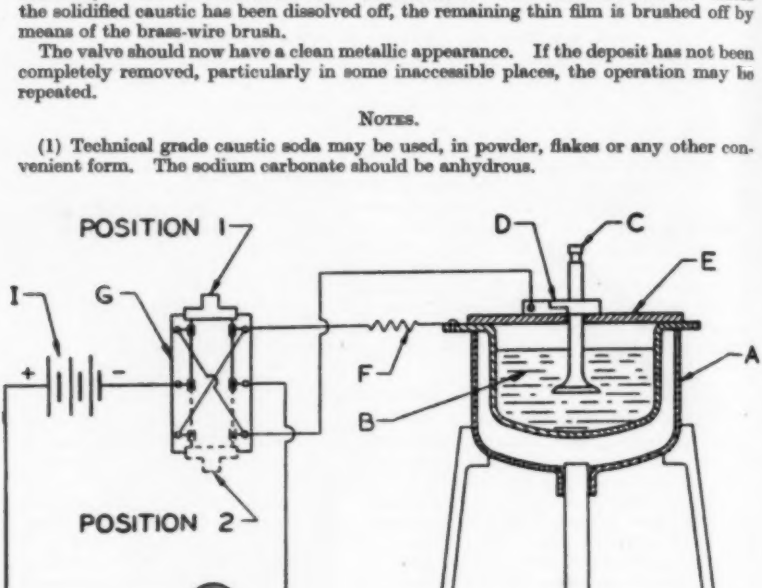



FIG. 1.

DIAGRAM OF THE EQUIPMENT

*A*—Melting Pot with Burner, 5¼-in. diameter, 3 in. deep (No. 15 melting-pot furnace, Johnson Gas Appliance Co., Cedar Rapids, Ia., fitted with a home-made lid).
*B*—Molten Electrolyte (60 weight-per cent of sodium hydroxide and 40 weight-per cent of sodium carbonate).
*C*—Valve to be Cleaned.
*D*—Clamp.
*E*—"Transite" Cover.
*F*—Resistance (0·5 ohm).
*G*—Two-Pole Double-Throw Knife-Switch.
*H*—Ammeter (0-30 amp., direct current, charge and discharge).
*I*—6-Volt Storage-Battery.

Switch Position 1, valve as cathode (normal position).
Switch Position 2, valve as anode (current reversed).

(2) No definite information is available regarding the number of valves which can be cleaned before renewing the melt. As many as 30 valves have been cleaned easily with one melt, but this number will no doubt vary with the type of valve and deposit.

(3) The solidified electrolyte will absorb moisture from the atmosphere and frothing may, therefore, be experienced when the bath is heated up again after standing. If a large amount of liquid collects on top of the melt it may be well to pour this off, adding up caustic soda and sodium carbonate approximately in the ratio of 60 : 40 if necessary to bring the level of the molten electrolyte up to about 1 in. from the top of the pot. Storing of the cooled melting pot in an airtight container, such as a laboratory desiccator, will obviate this trouble.

(4) To dispose of a spent batch of electrolyte, the *cold* pot is put in a sink, and water (preferably warm) is run directly on to the solidified melt by means of a rubber hose connected to the faucet.

(5) If the bath contains an appreciable amount of lead salts, or if the valve to be cleaned had a large deposit of lead compound, a thin grey film of lead may remain adhering to the steel. This can be removed by reversing the current for 10 sec. before removing the valve from the bath. In this case, the metal may take on a golden tinge which is probably due to a very thin coating of iron oxide. The double-throw switch illustrated in Fig 1. facilitates this operation. When only forgings, scaling specimens, and the like, are to be cleaned, this switch may be omitted.

### Discussion.

Separate tests made on polished specimens have shown that the loss of metal during the cleaning process is practically nil. Although the method, as described, is particularly adapted to the cleaning of exhaust valves, it has been found equally satisfactory with scaling specimens, and in removing forging scale.

### Precautions.

(1) Caustic soda causes very serious burns. The danger of handling it in the present work may come either from exposure to the powdered material when making up melts or, more seriously, from spattering of molten material. The operator should wear a laboratory coat with sleeves (not a sleeveless apron), gloves, with gauntlets, and goggles, whenever he is handling the caustic soda or opening the bath, whether to insert or remove valves or whether merely to inspect or stir the melt.

(2) The stirrer or any object which has been in contact with the melt will be covered with caustic soda. This will absorb moisture, and, if the object is put back into the bath without precautions, serious spattering may occur. It is best to insert the stirrer in the bath through the spout, before removing the lid, to confine any spattering which may occur.

(3) When a hollow-stem valve with driven-in plug was heated in the electrolytic bath in this laboratory, the plug was blown out, fortunately without causing any accident. Valves of that type are used only on some aircraft engines. They should be tested prior to cleaning by heating to 400° C. in a place where failure would cause no damage.

Salt or sodium-cooled hollow-valves, or other valves with welded-in plugs, can be handled safely.

## *DISCUSSION.*

THE CHAIRMAN said he was sure it would be agreed that the paper was a worthy successor to the one on "Ethyl" which Mr. Banks had presented to the Royal Aeronautical Society about two years ago. It was packed with invaluable information distilled from a wide experience.

Among many suggestions calling for discussion, some of them controversial, Mr. Banks had mentioned the need for inter-coolers and two-stage superchargers, and had given some most attractive fuel-consumption figures, which he was sorry to see had been culled from American practice. No one had a greater admiration than he himself for American practice, but he hoped that some of those present would take up the cudgels on behalf of the British aero engine.

With reference to the remark at the beginning of the paper: "The Americans taught us the importance of fuel quality and anti-knock value," it was true that the Americans had done a very great deal in that respect, but he thought it was only fair to recall that it was Mr. Ricardo who, about sixteen or more years ago, first pointed out that it was the detonation or anti-knock quality of a fuel which in the future would decide what that fuel was worth.

There were only two other points to which he wished to refer at the moment. One was the question of the correlation of anti-knock value in test engines and aero-engine cylinders. As the results of it had not yet been published, Mr. Banks did not mention in his paper the co-operative work on the subject which had been going on in this country, but it was right that that work should be mentioned. It was work in which the aero-engine designers, the fuel suppliers and the Air Ministry had been co-operating; the results of the investigation were now being made use of, and a specification would shortly be issued by the Air Ministry for 100 octane fuel. The outstanding need to-day in connection with this work was for some instrument which would give a positive, objective indication of the first beginning of destructive detonation. Hitherto those concerned had relied either upon a rise of temperature in the cylinder-head or upon audible detonation, but neither of those methods was satisfactory. He thought that the development in the last two or three years of the cathode-ray indicator would help more than anything else in the assessment of the value of fuels and their real behaviour in the engine cylinder. Several of those indicators were under development at the present time. There were certain difficulties associated with their application to high-duty engines, but he would like to say that the Air Ministry wished to give every encouragement possible to the development of such indicators, so that they might be made effective instruments for use on aero-engine cylinders. He hoped that one or two of those present that evening would give an account of the present position with regard to the development of the cathode-ray indicator.

He would ask Major Bulman, who was probably more intimately connected with the development of aviation engines in this country than anyone else, to open the discussion.

MAJOR G. P. BULMAN said that the primary duty of the individual privileged to open a discussion was to do honour to the author and to express the gratitude of the audience to him for his paper, so that those who spoke subsequently could devote their allotted span to tearing the paper to pieces or seeking to pump the author for more information! On the present occasion he addressed himself to his task with pleasure, and he could speak with absolute sincerity from a long knowledge and appreciation of Mr. Banks and his work.

Mr. Banks had come into the aeronautical world about nine years ago as the apostle and evangelist of St. Ethyl. He had been welcomed, because he had offered greatly increased power and efficiency, but it had not been long before it was found that ethyl was very much an acquired taste, and its arrival at the aero-engine works had soon been followed by the presentation of a large number of badly burned and unpleasant exhaust valves. The gift horse had indeed been looked at in the mouth. Mr. Banks, however, had tackled the difficulties constructively and with the utmost good will, and had become a guide, philosopher and friend to all concerned. He had shown his impartiality and independence (excellent in a scientific sense) by helping this country very materially to win the Schneider Trophy and the speed record by his work on fuel, and then going to Italy and helping the Italians to win back the speed record! The fact that he had never been able to obtain from Mr. Banks any real information about what he had done abroad and what the foreign engineers were doing, showed Mr. Banks' discretion, and gave one an absolute conviction that what he saw in this country remained locked up and did not go abroad. Among his other virtues was the fact that he served as an excellent ambassador between engineers in this country and their many American friends; he spoke both languages and he understood and exercised the respective senses of humour of the two countries!

It would be impossible, he thought, to exaggerate the importance of fuel in aero-engine development. Before the advent of the 87 octane spirit, aero-engine development had appeared to be becoming asymptotic in its curve, but the 87 octane fuel with ethyl introduced a fresh era, although a great price had had to be paid for it in the overcoming of its defects. Until then supercharging had been employed in the aero engine in maintaining ground-level atmospheric pressure intake conditions at an altitude, but the new fuel had made it possible for some appreciable measure of supercharging to be used for ground "boosting," and had thereby enabled the performance of aircraft to be improved materially.

A fresh impetus was now promised with the advent of the 100 octane fuel, fortunately at the right moment. The recent advance in aeronautical design had made it possible to produce aeroplanes of high performance which, once off the ground, could cruise at high speed with a relatively small percentage of power. The difficulty was to take off from the ground, and therefore the increase of take-off power which the higher octane fuel provided was particularly valuable. It must be remembered, however, that it was airscrew thrust, and not simply shaft horse-power which was required, and it was interesting to note that in a recent test of a particular engine a more effective take-off thrust was obtained by running the engine at a higher speed and 4 lb. boost than by running it at 6 lb. boost.

Mr. Banks in his paper had queried whether a two-speed airscrew would permit full advantage to be taken of the increase in power otherwise obtained. To a very large extent it seemed probable, by providing increased range between the two positions. Whereas the 87 octane fuel had given rise to many difficulties in developing engines to employ it—he thought Mr. Banks had been blamed unduly for some troubles that arose not from ethyl but from the higher power that ethyl enabled engineers to produce—it was hoped that there would be less fundamental trouble in coping with the higher-quality fuels, and already, with the existing engines, very marked improvement was offered. For instance, there was one standard type in which, without any alteration being made except that it was run at a throttle opening to give about 12 lb. per sq. in. boost instead of 5 lb., the power at ground level had been increased to over 1000 H.P. from the standard 700 H.P. That engine had been run on the bench for a little over 20 hours at this overload before anything had happened, and then the cylinder studs had begun to break. Another engine, of a different type, after it had been fitted with pistons of higher compression, had achieved a fuel consumption of 0·38 lb. per b.h.p.hr., the mixture being weakened merely to give the usual 3 per cent. drop in r.p.m. at cruising power equivalent to what was practically the maximum power on 87 octane fuel. Of course, much development work remained to be done to ensure that those engines would continue to maintain such higher powers and reduced fuel consumptions under the current standards of reliability and overhaul life.

There were so many points in the paper which many present would wish to discuss, but there were a few that he himself would like especially to mention. Mr. Banks suggested that the two-speed blower was merely a passing phase. He disagreed with that; he thought that, quite apart from any advance in fuel quality which might come about in the future, the two-speed blower would earn its keep from the point of view of economy in cruising; one would cruise on the low-gear supercharger running at full throttle at that height intermediate between the two rated altitudes, giving the appropriate economic cruising power for the engine, saving thereby the power wasted in driving the high-speed supercharger, and running under full throttle carburettor conditions, worth together probably a 10 per cent. advantage in fuel consumption.

He agreed with the Chairman in feeling that Mr. Banks had unduly emphasized the economy of the American engines. He accepted the American figures and admired them, but he did not think that the fact that British figures had not been published implied automatically that the British figures must *ipso facto* be worse than the American ones.

He was sure Mr. Banks would not claim that the idea of the flat engine was entirely his own. It had, of course, been thought of by many, the difficulty being how to make a truly flat engine enclosed in a wing. He was very doubtful whether it was worth while to make the attempt, unless the whole engine could be contained within the envelope of the wing, without any excrescence. Such an engine too must be designed in the closest co-operation with the aeroplane designer.

MAJOR BULMAN wrote subsequently:

Experience so far in the Royal Air Force has not confirmed certain apprehensions that cold corrosion due to tetraethyl-lead would be troublesome. It is true that a number of engines stored in this country for a few weeks only after delivery, when partly dismantled for another reason were found to contain a number of cylinder barrels (nitrogen hardened) of disturbing appearance, but the practical deterioration was found to be negligible: moreover, many engines, not specially examined, but of the same period and almost certainly the same internal condition, had gone into active use without arousing comment or suspicion in their running, or reduction in overhaul life. However, the employment of a protective medium such as E.G. 174 is a wise precaution if a sharp epidemic induced by particular climatic conditions is to be avoided.

In regard to drag, the author appears to be unduly pessimistic in estimating that the air-cooled engine in general, as distinct from the particular form of the large-diameter single-row radial, is likely to be inferior to the liquid-cooled installation to the extent of 30 to 40 m.p.h. at speeds of 300 m.p.h. and over. Nor does one agree that 1500 H.P. is likely to mark the useful maximum power of the air-cooled type, either for civil or military use.

It is probably fortunate, for the ultimate progress of the aero engine, that 100 octane fuel has not so far been produced, nor may indeed arrive for some time, in sufficient and certain quantity to justify general Service adoption. Much remains to be done in engine development to wring the most out of 87 octane fuel; work thus devoted will contribute to a greater leap when the 100 octane fuel really matures. A non-detonating fuel may cover a multitude of engine sins, and corrupt good design manners. Let there be no doubt, however, that petroleum technologists and fuel research workers now have the opportunity to provide by their efforts an advance in aero-engine development, with its effect on Air Power, which the engine designer by himself cannot hope to offer by any other means.

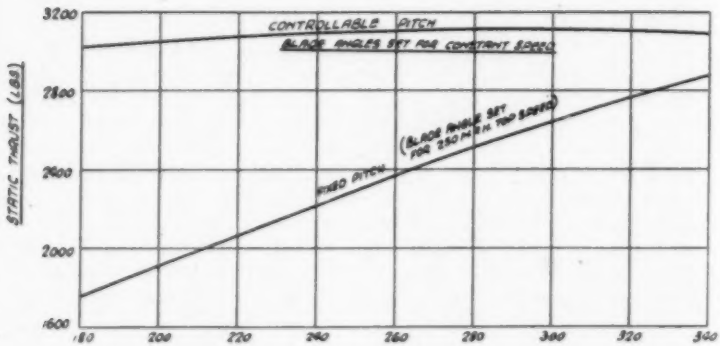
THE CHAIRMAN remarked that the question of take-off thrust and take-off power which had been mentioned by Major Bulman was of primary importance to those concerned with aviation, and he would ask Mr. F. M. Thomas of the de Havilland Co. whether he would care to say something on this matter.

MR. F. M. THOMAS said that the paper was such a comprehensive survey of the subject and contained such a large number of imposing data that one felt a certain timidity in disturbing it. He nevertheless considered it advisable to remind those present that there was really no point in giving more power for take-off unless that power was directly transferable into thrust. Usually all the power additions did not become thrust because the airscrew efficiency was so susceptible to blade angle changes that when one put in more power one lowered the efficiency and even lowered the thrust in some cases. The sequence of arguments leading to that conclusion was rather involved, and he would therefore illustrate it by means of slides. All the charts were calculated for one typical modern high-powered engine.

Fig. A showed the variation of static thrust with brake mean effective pressure. The b.m.e.p. figure was used instead of power because the former was more directly related to an improvement in the fuel. It would be seen that with a fixed pitch airscrew there was a consistent gain in thrust with increase of b.m.e.p. The controllable pitch airscrew at each point was set to such an angle as to absorb the added power and there was very little increase of thrust in that case. Most of the new engines had about 180 lb. per sq. in. b.m.e.p. to start with, and an increase of 30 per cent., which the new fuel permitted, would bring the figure up to about 235 b.m.e.p. As a result of this gain in power the controllable pitch airscrew

FIGURE A

VARIATION OF STATIC THRUST WITH B. M. E. P. FOR FIXED & CONTROLLABLE PITCH AIRSCREWS.
3-BLADE AIRSCREW 12·6 FT. DIA



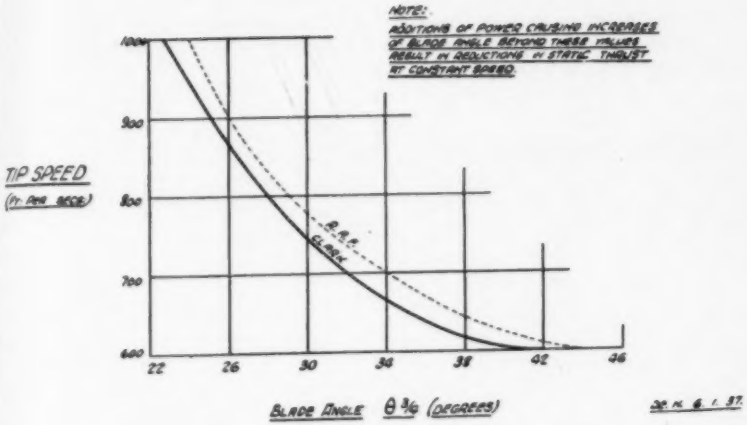

would gain very little in thrust. The fixed pitch airscrew gained considerably because its blade angle was from the start set at a badly stalled value.

Fig. B showed the variation of airscrew tip speed with the blade angle for optimum static thrust conditions. At any given tip speed it was not advisable to put in more power if the increase resulted blade angles larger than those shown.

The third slide (Fig. C) was a considerable elaboration of the first slide. It showed the variation of static thrust with b.m.e.p. at various engine speeds. The right-hand portion of the chart was included, even though it showed impracticably large pressures, in order to illustrate the trends most clearly. Choosing any one r.p.m., as one increased the b.m.e.p. from the values of ten years ago to the present-day values there was an improvement in static thrust, but the developments in that direction during the next ten years would not be so useful, if his calculations were correct.

FIGURE B

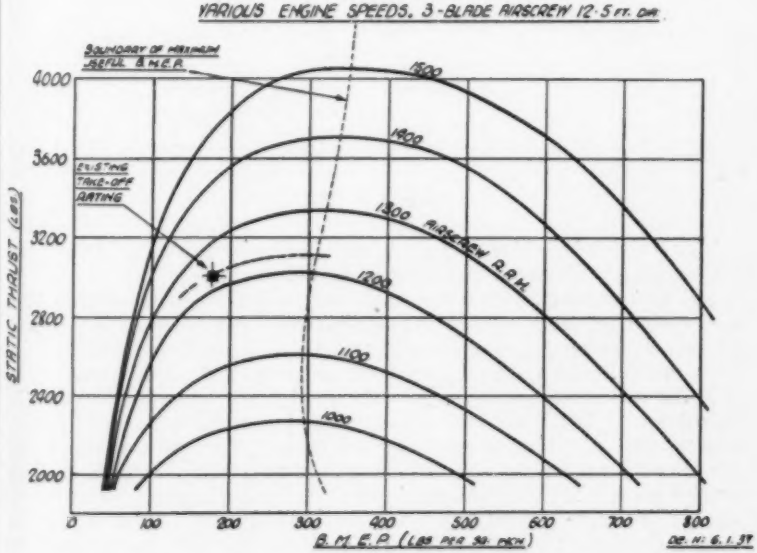
VARIATION OF TIP SPEED WITH BLADE ANGLE AT OPTIMUM STATIC THRUST CONDITIONS.




DR. H. 6. 1. 37.

FIGURE C

VARIATION OF STATIC THRUST WITH B.M.E.P. AT VARIOUS ENGINE SPEEDS. 3-BLADE AIRSCREW 12·5 FT. DIA.




DR. H. 6. 1. 37.

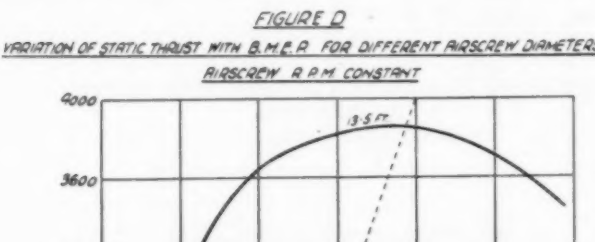
In fact, it appeared to be a general conclusion that the gain in static thrust due to *iso*-octane fuel was small no matter at what speed the airscrew turned.

An interesting point about the curves shown in the slide was that a very large increase in thrust was obtained at high values of b.m.e.p. due to an increase in airscrew speed. It was well known to-day that a static thrust could be most easily improved by using a two-speed gear, but it was interesting to see that this expedient became more advantageous and necessary at high b.m.e.p.'s.

FIGURE D

VARIATION OF STATIC THRUST WITH B.M.E.P. FOR DIFFERENT AIRSCREW DIAMETERS

AIRSCREW R.P.M. CONSTANT




DE H. 6 / 37

Fig. D showed that large improvements in thrust could also be obtained by varying the diameter, especially at high b.m.e.p.'s.

Mr. Thomas emphasized that these curves illustrated calculations on one engine but that similar calculations on many other high-powered engines showed corresponding trends; and that during the past five years numerous full-scale tests had borne out the methods of calculation.

If the curves were to be taken seriously, it must be argued that static thrust was an important item in take-off, and he thought that was so. It was not the only thing to be considered, because the thrust at the end of the take-off was a little more influential. Calculations of the same nature carried out on the thrust at the middle of the take-off and again at the end showed the same general trend, *i.e.*, that one did not get full return for large increases in take-off power. The optimum points, however, occurred

at higher b.e.m.p.'s as one reached higher air speeds; also, near the end of the take-off increases in revs did not produce such large increases in thrust as they did at the beginning.

He thought that the higher-quality fuels should be used not primarily to obtain boosts for take-off, but rather to raise the whole rating of the engine, especially if the gain was obtained through increase in compression ratio. He thought one would have a better aircraft in every respect if the cruising and maximum powers as well as the climb and the take-off powers were increased by a moderate amount than one would have if the take-off power only was increased by a very large amount and the other conditions remained the same.

Mr. C. H. BARTON read the following comments from MR. E. L. BASS :

Mr. Banks has referred in his paper to the question of correlation of the results from fuel-testing units and full-scale engines.

A number of experiments which we have carried out on single-cylinder aero engines using fuels of different composition have shown that the relative knock-ratings of fuels vary appreciably according to the mixture strength. That is to say, at full rich or take-off mixture strength the relative knock-ratings of fuels of varying composition will be different from those under weak or cruising conditions. It seems important, therefore, to decide under what mixture strength conditions fuel-testing on the knock-rating engine should be conducted. The present method whereby the mixture strength is adjusted merely to give "maximum knock" appears to be the least satisfactory one that could be devised, because in actual fact there are no means provided for determining exactly the mixture strength which is being used.

In view of the fact that it is possible to obtain different relative knock-ratings for fuel under weak and rich mixture conditions on the full-scale engine, it may be necessary to obtain knock-ratings under a similar range of mixture strengths on the fuel-testing engine, and experiments will have to be conducted to find some arbitrary variation between the two ratings which must not be exceeded.

Mr. Banks also referred to the use of a thermo-couple embodied in a sparking plug, and I should mention that our Research Laboratory at Delft has developed such a unit. The arrangement is shown in the diagram attached. In a paper recently read by Mr. Boerlage before the Chambre Syndicale des Industries Aéronautiques in Paris, some results obtained with such a plug were given, and one of the curves is reproduced herewith. These tests were made on a single-cylinder Bristol "Pegasus" engine. It is interesting to observe that in comparing a fuel which does not detonate at all with one which commences to detonate as the mixture strength is reduced, there is a breakaway of the temperature curves as given by the sparking-plug thermo-couple, at the point at which incipient detonation was observed aurally. The disadvantage of the sparking-plug thermo-couple may lie in the fact that the temperature of the plug itself may vary quite considerably according to the fit of the threads in the sparking-plug adaptor, and whether or not they are perfectly clean. However, this should not be a serious disadvantage if, when using this type of thermo-couple for fuel testing, the results are always referred to those

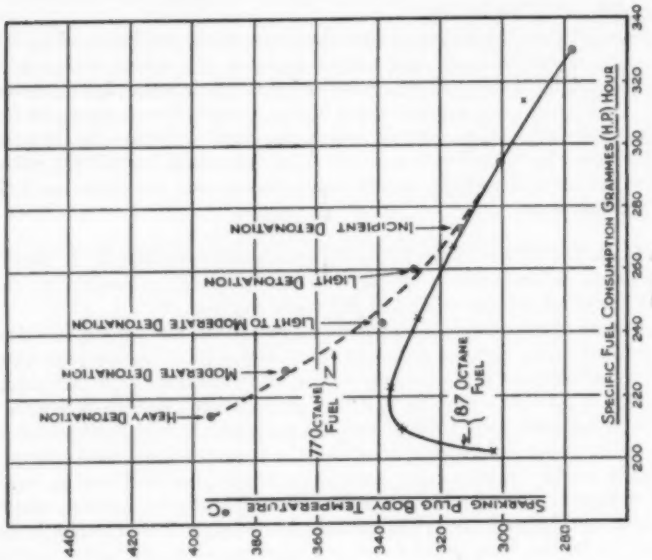

Specific Fuel Consumption Grammes (H.P) Hour
200
220
240
260
280
300
320
340
Sparking Plug Body Temperature °C
280
300
320
340
360
380
400
420
440
87 Octane Fuel
77 Octane Fuel
Incipient Detonation
Light Detonation
Light to Moderate Detonation
Moderate Detonation
Heavy Detonation

Fig. 2.

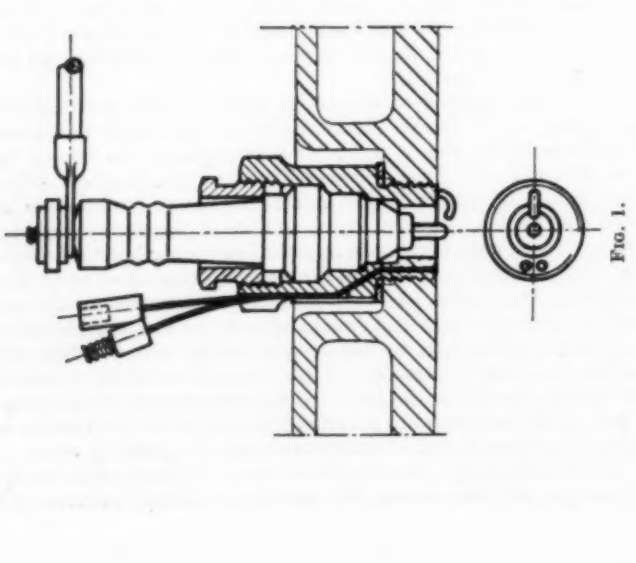


Fig. 1.

obtained from a fuel of sufficiently high anti-knock value to ensure that no detonation occurs. Failing the advent of a really satisfactory electric indicator, the sparking-plug thermo-couple seems a rather more delicate means of detecting detonation than any other means available at the present time. It might be added that our Delft laboratory has already had experience with this particular design of thermo-couple working at high output and temperatures for over 75 hours, and the results have been entirely satisfactory.

With regard to the effect of calorific value on fuel consumption and operating costs, calculations show that for aircraft with a range of five hours in still air, cruising at 1300 H.P. on 87 octane fuel, a reduction of 10 per cent. in the calorific value of the fuel would mean that the additional weight of fuel which could be carried would amount to 450 lb. or 7½ per cent. of the weight of the engine, fuel and tanks. In some existing aircraft this may mean that 10 per cent. of the payload will have to be sacrificed.

In conclusion, I should like to thank Mr. Banks for an extremely comprehensive paper, which will be used, together with his previous paper to the Royal Aeronautical Society, as a reference work on many occasions.

Mr. H. Wood said that Part I of the paper, which dealt with fuels, fuel rating and correlation, indicated the extent to which the fuel companies were helping in the improvement of the internal-combustion engine. His own Company, Messrs. Rolls-Royce, had carried out extensive fuel testing on aero-engine cylinders in order, first, to ascertain the response of their type of engine to the various fuels proposed from time to time, and secondly, to investigate the engine problems relating to the efficient use of fuels of high knock-rating. Some of those fuel tests had been done for the Air Ministry, and he had their permission to state some generalized conclusions.

His Company's method of testing covered the behaviour of the fuel under the practical conditions of cruising and take-off, *i.e.* of weak and rich mixture running, the weak mixture being that corresponding to 8 per cent. power drop, and the rich mixture to that beyond which power began to fall. In both cases an intensity of aural detonation of 20 ft. was selected as the standard of comparison. Unfortunately, they still had to use that, because they had not yet been able to obtain satisfactory indications with the cathode-ray indicator. The tests were carried out under constant engine conditions of speed and jacket temperature, and the variables under control were the charge pressure and the temperature.

The generalized conclusions arrived at were that all the hydrocarbons generically known as petrols were very sensitive to charge temperature for both weak and rich mixtures. In the case of weak mixture running, all such fuels tended to a common low b.m.e.p. at charge temperatures of the order of 130° C., but they had different rates of appreciation as the temperature was reduced. It was the experience of his Company that the aromatic fuels had a considerably greater rate of appreciation than the aromatic-free fuels. For rich mixture running there was less sensitivity to charge temperature, and the various fuels showed more individual characteristics, while again for his Company's engine the aromatics were better than the non-aromatics of the same knock-rating.

The various blends of *iso*-octane shared the unfortunate weak mixture

characteristic to which he had referred, and for the aero-engine builder and for aircraft operation generally that feature imposed serious limitations. The prospect, however, was not hopeless, because it had been found that the degeneracy to a common low power at high charge temperatures was not shared by two other groups of fuels. One mentioned by the author, blends of *iso*propyl ether, gave a very substantially higher m.e.p. at the 130° C. for weak mixture running and an m.e.p. so high for the rich mixture case that it was above the safe limit of running for the test cylinder.

He had not been able to make alternative blends of *iso*propyl ether to explore its possibilities, but he would like to do so, because the disadvantage of reduced calorific value and consequent increased consumption required examination. That disadvantage, however, was not a direct arithmetical one, because the greater immunity from detonation and the higher m.e.p. thereby made possible automatically reduced the consumption differences. Another feature which was useful in the case of *iso*propyl ether was a substantial reduction in maximum pressures obtained.

The other group of fuels, to which the author had only partly referred, was a mixture of alcohol derivatives, and those, he thought, very definitely came into the picture, because of their wonderful lead response which was maintained to a straight line law on his Company's engine up to 6 c.c. per gallon, which was the maximum they had tested. The particular blending agent tested was a mixture of ketones prepared by the Distiller's Co. and characterised by physical properties differing from the more general alcohols but more advantageous as an engine fuel. They had tested this blending agent with aromatic and non-aromatic fuels in varying percentages and with varying lead additions. The lead response depreciated as the petrol in the mixture was increased, proving, he thought, that it was the ketones which had the good lead response. But a blend of 50/50 of the agent with D.T.D. 224 or with D.T.D. 230 both leaded up to 4 c.c. per gallon gave results similar to but appreciably better than *iso*propyl ether, with again the aromatic mixture appreciably better than the aromatic-free blend. Similar remarks about consumption as for the *iso*propyl ether applied to these blends, but with greater possibilities of bridging the gap. They also had the same advantage as the *iso*propyl ether in that there was a considerable reduction in the maximum pressures.

A few observations could be made on lead response. All the hydrocarbons which his Company had tested showed diminishing lead response with increase of lead content. Straight *iso*-octane showed on their engine the greatest response to the first 2 c.c. of lead of any fuel tested, but the rate of response diminished rapidly with increase of lead. He had no experience of *iso*propyl ether, having so far tested only one blend. The ketone blends to which he had referred had a lead response curve which appeared to be a straight line in terms of m.e.p. up to 6 c.c. being of the order of about 25 m.e.p. per c.c. of lead for weak mixtures and 35 m.e.p. for rich mixtures at temperatures of about 130° C., which was very good indeed, but these rates would vary with different engines and with the same engine under different operating conditions.

The foregoing results showed, he thought, how difficult fuel rating became when considered in relation to actual engine performance. Taking fuels of the same C.F.R. knock-rating, his Company had recorded differ-

ences on the aero-engine single cylinder of as much as 80 m.e.p. under identical conditions of running. They had confirmed single-cylinder differences in the case of two fuels of 77 knock-rating on the complete engines, and they would very much like to have an opportunity of seeing whether similar differences were confirmed in the case of fuels of 100 knock-rating.

He thought the remarks in the paper on maximum power production might be modified with regard to the effect on power of charge temperature by a consideration of the improvement of performance at high temperatures made possible by the two blending agents to which he had referred.

Mr. E. M. Dodds said :

In view of the difficulties of correlation between the C.F.R. Motor Method and aircraft engines, it would seem that any effort in the direction of trying to obtain an average rating on the C.F.R. is of little value, by virtue of the extremely large discrepancies which exist between the ratings given by aero engines themselves. A more promising line of investigation might be to develop a separate C.F.R. technique to correlate with each aero engine under each set of normal running conditions. Thus it might be possible to choose C.F.R. conditions to correlate with liquid-cooled engines at cruising power, another set of conditions to reproduce fuel tests at take-off power, and similarly for air-cooled engines. The duplication of C.F.R. tests required might not, after investigation, be as complicated as would at first appear, and would be more convenient and less expensive than conducting frequent fuel tests on individual single-cylinder and complete aero engines. Many of the possible variables on the C.F.R. engine are easily adjusted, *e.g.* jacket temperature, intake temperature, ignition timing, throttle opening and intensity of detonation.

Perhaps the last is the most important of these. It does not seem logical to rate fuels under the present standard knock, which is of comparatively large intensity, when fuels are rated on aircraft engines at incipient or slight detonation. This leads us to the question of measuring incipient knock on the C.F.R. For this purpose we have found our cathode-ray indicator to give promising results as a knockmeter. The pressure element used in our indicating equipment is of the capacity type, and consists only of steel and mica, which need not even be water-cooled, as the diaphragm is supported against engine pressures. This element is very robust from the mechanical point of view, and excellent thermally. Diagrams representing either pressure-time or rate of change of pressure against time are obtained directly from this element by means of a straightforward amplifier. In this connection it should be pointed out that both pressure element and amplifier should possess a flat frequency response to at least 50,000 cycles per second, if accurate oscillograms are to be obtained under conditions of detonation. Although up to the present time no really satisfactory pressure-time card has been obtained on a boosted aircraft engine, the instrument described above at least gives an excellent measure of detonation in the cylinder, either incipient or comparatively heavy.

Since change of capacity is the method adopted, the instrument obviously opens up very wide possibilities in the direction of obtaining oscillograms of either motion or velocity of moving parts, by simply arranging an

insulated plate at a short distance from the moving part. In this way diagrams showing valve lift, tilting of the flywheel, snatch in bevel gear drives, etc., etc., are readily obtained.

In addition to satisfactorily indicating knock in an aircraft cylinder, into which a pressure element is screwed, we have also succeeded in indicating knock by simply forcing the insulated lead which normally connects with the pressure element between the upper fins of the Bristol engine. Excellent results have also been obtained on liquid-cooled engines by resting an insulated plate on a sheet of mica over a suitable part of the cylinder head casting. For this work a time base is not really necessary, so that our new knockmeter can be used on an aircraft engine without the necessity for having anything whatsoever connected to the engine. The advantages of such a method are obvious to everyone. All that is necessary in the case of the main engine, for example, is to obtain detonation oscillograms from each cylinder in turn, so as to determine which is subject to the heaviest knock, the lead then being left between the fins of that cylinder for subsequent fuel tests. Calibration would be performed in the ordinary course of events on the similar single-cylinder test unit, and the results on the multi-cylinder job could then be evaluated. It is hoped in the near future to produce a simplified, compact and light-weight version of this instrument, involving either a suitable meter or, preferably, a miniature cathode-ray tube, which could be fitted in the cockpit of a machine, enabling the pilot to detect detonation long before it becomes audible to him and, therefore, destructive in character. A simple instrument of this character has also a number of possibilities for use as a C.F.R. knockmeter under conditions of either standard or incipient knock intensity, without the necessity for having a pressure element in the cylinder head.

MR. W. W. WHITE said he thought that Mr. Banks' description of the highest octane fuels was particularly interesting, and it might be of interest to engine designers to consider the availability of high octane number fuels. *iso*-Octane was very suitable, as everyone knew, and it was available in large quantities, but it was not available in limitless quantities. *iso*-Propyl ether, on the other hand, could be made available at short notice in what amounted to limitless quantities, if one considered the consumption likely to occur in aviation fuels during the next few years. Mr. Banks' point that *iso*propyl ether as a blending agent could be used as a complementary source of supply of blending agents needed to manufacture fuels of high octane number, rather than to displace *iso*-octane, was worthy of consideration by everyone interested in the subject.

MR. O. THORNYCROFT said he would like to refer once more to the history of the recognition of fuel anti-knock value. The Chairman had reminded Mr. Banks that many years ago Mr. Ricardo had stated that the most important characteristic of a petrol was its resistance to detonation. He himself had worked with Mr. Ricardo for a great number of years, and he felt sure that Ricardo would like it to be stated now that earlier still, actually in 1906, Professor Bertram Hopkinson had appreciated the existence of detonation in an engine.

Hopkinson was then working at Cambridge; Ricardo assisted him in his

experiments, and he found, in a spark-ignited homogeneous charge engine, that the indicator occasionally blew up. When this was investigated it was found that the conditions under which the indicator was sometimes damaged were those in which a sudden pressure rise occurred near the end of the combustion period. Hopkinson then showed that this sudden pressure rise was a phenomenon quite different from pre-ignition, or ignition commencing before the passage of the spark at the igniter.

Mr. Banks had said that the Americans taught us the importance of fuel anti-knock value. Would it not be truer to say that the Americans had appreciated, and had applied more quickly than we had done in this country, the discovery of lead ethyl as an anti-knock agent? Even in the U.S.A. it took three or four years to bring lead ethyl into practical use in aircraft fuels. In this country, due no doubt to a policy of caution, it had taken considerably longer.

He would like to take this opportunity to say that he considered Midgley's discovery of the effect of lead ethyl was one of the outstanding discoveries of the age. In one respect, however, he was sorry that lead ethyl had appeared, for, by raising fuel anti-knock value by about 10 octane numbers, it had, for the present at any rate, put the compression ignition oil-engine out of court—although only just out of court.

Mr. Banks had suggested in his paper that rotational swirl of the charge in the cylinder might be of advantage in spreading combustion in such a way as to inhibit detonation. The photograph shown of a piston top exhibited very clearly markings which could only have been produced by rapid translational movement of the burning charge. Mr. Banks, however, did not say whether this engine had shown a high or low tendency to knock.

He had himself been concerned in certain experiments which showed that swirl in a spark-ignition engine could be definitely objectionable. In two rather similar air-cooled engines the relative rates of swirl were measured by blowing air through the inlet valve of each cylinder with the piston replaced by an anemometer. The rotational speed of swirl was found to be three times as high in one cylinder as it was in the other. The difference was evidently due to a difference in the degree of asymmetry in the passages leading to the inlet valves of the two engines. The engine with the high swirl had suffered badly from hot pistons and stuck rings, while the other had not.

There was, moreover, evidence that very high swirl in a spark-ignited engine tended to reduce the combustible range—in other words, it made the engine " sensitive " to mixture strength. Lastly, where swirl had been extremely high, the consumption of lubricating oil was found to be high, and was increased and diminished as the swirl was raised and lowered respectively.

He thought there was much to be said for low swirl in a petrol engine, and he would go further, and say that even general turbulence should be kept as low as was consistent with the proper spread of inflammation. If the turbulence was unnecessarily high there seemed little doubt that the heat loss and the surface temperatures were increased, a condition to be avoided particularly in an aircraft engine.

Mr. E. S. L. Beale said he wished to make a few very brief remarks about the cathode-ray type of indicator. He had been concerned with

developing one of those indicators, and it had been found that it was very much more difficult to apply them successfully to aircraft engines than it was to apply them on heavy engines such as would be used for road work and so forth. He thought the chief reason for that was the increased mechanical vibration which occurred at the top of a thin aircraft cylinder; in such a position the indicator was subject to enormously high accelerating forces of high frequency, and that certainly did make things more difficult. Whatever was used to measure the pressure must have some mass. It might be a diaphragm backed by a carbon-pile or a quartz crystal, or it might be a diaphragm alone, as in the Standard–Sunbury indicator, but whatever it was it must have some mass, and if it was subjected to very high accelerations it was bound to deflect and produce effects which would appear to be pressure variations, but which were actually a measure of the vibration. In conjunction with the Anglo-Iranian Oil Company he had done a great deal of work to try to reduce the effect of vibration and other spurious effects on the pressure unit, and he thought they had succeeded to a large extent, because, as Mr. Banks had mentioned, they were able to use the rate-of-change of pressure diagrams also, even though the overall high-frequency response of the system was good. He was convinced that that was an extremely important thing.

Much useful information could be obtained from a pressure diagram which was an accurate one at high speeds, but on the rate-of-change of pressure diagram (provided that it was a true one) a great many things could be seen which could not be seen at all on a pressure diagram. Most of the effects in which one was more particularly interested nowadays, such as detonation effects and so forth, were high-frequency vibrations, and those could be seen on a rate-of-change of pressure diagram when they could not be seen at all on a pressure diagram. In other words, the important high-frequency effects were greatly magnified on the rate-of-change diagram, which was, of course, why it was so difficult to design a unit which would give a satisfactory rate-of-change diagram.

One of the difficulties which was experienced was to interpret the rate-of-change of pressure diagrams, because one was not familiar with it, as the old-fashioned type of indicator gave only an ordinary pressure diagram. The rate-of-change diagram was also liable to be very much complicated by other high-frequency effects in which one was not particularly interested, but with a little ingenuity in the use of attenuators and simple filters in the electrical circuit the unwanted effects could be eliminated, or reduced in amplitude, leaving the wanted effects on the diagram. He was convinced that it would be found that rate-of-change of pressure diagrams were very important.

Work was being carried out at Sunbury on another method of detecting incipient detonation, which did not use the cathode-ray indicator at all, and personally he thought that that was the method which was likely to be finally adopted. One saw too much on a cathode-ray tube: one saw everything that was going on, all at the same time, and it was difficult to differentiate the various things one saw. What was required was some method that would tell one that the degree of pinking was so much, given by the steady reading of a pointer on a scale. One of the methods they had been working on was to measure the actual elongation of the cylinder walls due

to gas pressure on the cylinder head, as there were indications that this was one of the more important features of pinking. By the use of electro-magnetic pick-up units, of exactly the same type as were used on their cathode-ray indicator, they obtained electrical indications of change of length of the cylinder walls which could be amplified, rectified and put on to a pointer instrument. Actually they had found it advantageous in this case also to use rate-of-change of elongation instead of the elongation itself, and this was just what was given by the electro-magnetic unit.

The cathode-ray indicator was very valuable in enabling one to see what it was which had to be measured, but in this case a heavily damped pointer instrument was better for the final instrument.

Mr. G. H. Coxon asked how the Air Ministry was going to specify 100 octane fuel and how it was going to be tested. He did not think the supply companies yet knew exactly how to deal with it. Those with very extensive laboratories might be able to do so, but if the fuel had to be manufactured in an ordinary refinery and had to be tested there, he did not know any means whereby that type of fuel could be satisfactorily tested, bearing in mind the requirements of different types of engines and the different characteristics of possible fuels.

People talked very glibly about 100 octane fuel to-day, but he would like to know where it was all coming from. Only one country in the world to-day was producing *iso*-octane, and he wondered whether it was wise to design aircraft for a fuel which could be procured only from certain places and under peace-time conditions. He did not know what would happen to those machines if war broke out. In the United States the problem was quite a different one, and the American Air Ministry was probably right in developing its conditions to suit the raw materials in that country, but, speaking from the British point of view, he knew of nowhere to-day where one could get *iso*propyl ether or *iso*-octane outside the United States. There might be one or two other places in the world from which it could be obtained. Taking a typical example, the Air Force, where would the Air Force get the fuel from? He thought that those in authority should give very serious consideration to the question of designing engines to suit a theoretical type of fuel which he did not think would be available in practical quantity in time of war.

With regard to the development of the engine, could no attempt be made to develop an engine which would use the lower octane grades of fuel? Was an effort being made to develop what might be called the solid injection engine? How far could such a development go in increasing efficiency while using the ordinary grade of aviation generally available. Surely the factor of higher calorific value counted. That was a line which might well be followed, it seemed to him, rather than concentrating on 100 octane fuel, regarding which, as a war-time problem, he himself was rather afraid.

Mr. L. Pomeroy, Jr., said he had been a little disappointed, in reading Mr. Banks' paper, to see that under the heading of "Engine Development" sparse mention was made of the possibility of developing engines to run on low octane fuels. Mr. Banks was, of course, specifically interested in

higher octane fuels, but he thought it would be of enormous commercial and military value if high m.e.p. could be coupled with the use of low octane fuel, and in that connection he felt that Mr. Banks had been rather callous in his treatment of the hot exhaust problem. It might well be that, from the mechanical point of view, one could make the temperature of a valve too low, so that it would not respond to distorted seating, but surely the logical thing to do was to apply distortion of the seating or to try another form of valve.

He had been greatly impressed with the work which had recently been done in some quarters on engines with abnormally cool piston-chambers, particularly those with rotary valves, and engines of such a nature could be made to give very high m.e.p. on small cylinders—over 160 m.e.p. with 65 octane fuels, without boosting. That, he thought, was the line of development which should be followed up, and it was particularly significant because such engines seemed to derate completely the high octane fuels; in other words, changing over to high octane fuel did not give any tangible results. Therefore he felt that if by some means the poppet valve could be taken out of the system a great step forward would be made in engine design.

MR. MEYER said:

Since some speakers in the discussion have been advocating the use of fuels of lower instead of higher anti-knock value, I should like to give the opinion of the K.L.M. on this matter.

We expect that commercial flying in future will take place at higher altitudes—let us say at 25,000–30,000 ft. instead of 10,000–12,000 ft. as practised nowadays. With the increase of cruising altitude the b.m.e.p. will be decreased, and therefore the octane number of the petrol to be used during cruising will also be decreased. As you know, it is the practice that the expensive high-quality petrol is used only during take-off and first climb, and in case of emergency, when one engine has to be stopped during flight, whilst the cheaper fuel can be used during cruising. It is therefore interesting to know whether the rate of decrease of the minimum required octane number for the high-powered engines, now in use, can be estimated when increasing the cruising altitude, and if the cost of the fuel to be used in these circumstances can be appreciably diminished. With regard to this question it is also of importance to know if you consider it possible that in the distant future low-grade fuel could be mixed during flight with a high-grade one, or with special anti-knock dopes in various proportions, in order to obtain different octane fuels at varying altitudes.

When reading the preprint I learned many interesting things about the difficulties encountered in the construction and operation of modern high-powered engines. I felt, however, that a very important point had not been treated, which should be an interesting subject of discussion, when in the very last sentence of the paper I found that it had purposely not been mentioned. I refer to the lubrication of high-powered engines.

We are of the opinion that the development in the very near future is restricted not so much by the material and fuel, as by the lubrication of the cylinder walls, and we think that great attention has to be paid to it.

Although in our Company we have very favourable and long periods

between overhaul, these periods are mainly limited by piston-ring sticking. It is therefore necessary that, in the first place, the oil manufacturers provide us with a still better lubricating oil, but, on the other hand, it seems that attention has also to be paid to the construction of the piston rings, piston-ring grooves and to the clearances to be allowed. The deformation of the piston during the running of the engine has probably much to do with the subject, and also the choice of the material and the form of the rings themselves have a great influence on the sticking.

Piston-ring sticking is certainly not prevented by high oil consumption. We have found 1000 H.P. engines working under very satisfactory conditions with oil consumptions of only 2 litres per hour and 875-H.P. engines with consumptions of only 1·25 litres per hour.

The piston-ring sticking limits not only the period between overhaul, but limits also the petrol consumption of the engine. When flying with low specific consumption (even not as low as mentioned in the paper) we have not any trouble due to valve burning, detonation or spark-plug failure, but only of stuck rings. I want to say that we have tried out many lubricating oils, and that those which we are using in our engines may be reckoned among the best available. We therefore suggest that the point must be taken into consideration by the lubricating-oil manufacturers as well as by the engine manufacturers.

In connection with fuel economy, to which we are glad to see so great an importance attached, we are interested to know whether exact measurements of consumption have ever been taken during flight by any airline operator or engine manufacturer. Most of the records delivered by the engine manufacturers are based on test bench running, and do not correspond with the results obtained during flight.

Twice, by K.L.M., exact readings have been recorded. The first time, we needed these records for the Transoceanic flight of our plane *Snip*, which had to fly over water for a distance of 3600 km. (2250 miles). Special charts were drawn, from which the crew could determine, at each point of their flight, the altitude and speed—wind condition taken into consideration—giving the greatest radius of action. The second time the measurements were done on our new DC-3 plane, because on the regular lines also the crew ought to be in possession of such a chart, not only for making use of in case of emergency, but also for economizing as much on fuel as possible, by their method of flying. This point is perhaps of still greater importance than exact mixture control or increase of engine efficiency.

Dr. A. J. V. Underwood said he would like to refer very briefly to the point raised by a previous speaker with regard to the availability of high octane fuels. It was quite true, of course, that *iso*-octane and *iso*propyl ether were essentially products of the petroleum industry and their production was therefore restricted to those countries in which natural petroleum resources were available. He would point out, however, that there was another group of materials, which Mr. Wood had mentioned and which he had found to be even better than *iso*-octane or *iso*propyl ether. That group of compounds could be made by synthetic processes from coal, and for that reason were of particular interest for this country.

Mr. J. H. Millar asked whether Mr. Banks could give any figures as to the petrol consumption when turbo superchargers were used as compared with the petrol consumption when the more ordinary type of superchargers, mechanically driven, were employed.

The following written contributions to the discussion were received:—

From Mr. E. Ploix:

1. *Measurement of Octane Number.*

Mr. Banks showed that three methods are at present in use for measuring the octane number of fuel: the C.F.R. Motor Method, the C.F.R. Modified Motor Method and the American Army Method, these three methods being good ones, but each of them producing a better correlation in practice with a series of particular cases.

It was pointed out that the differences of correlation in these results arose largely from the test conditions, such as the mixture temperature and speed of operation, etc.

It would appear—and our own experience of the utilization of fuel of different origins in different parts of the world confirms it—that the origin of the fuel plays an important part.

In addition, the measurement of octane number under "heavy" detonation instead of under incipient detonation is, we think, another very important cause of error.

Finally, on carefully examining the methods of carrying out these tests, it is found that they are, generally speaking, far removed from reality; the mixture strength is that for maximum detonation, etc. . . . instead of being that for maximum power, etc. . . .

It seems, however, very difficult to effect these measurements in exact conformity with reality; for it would be necessary, in view of the fact that each engine reacts in a different fashion to the fuel, to test with the full-scale engines themselves, which is clearly impossible.

It would seem, however, desirable that the method and the standard test engine should approach as near as possible to reality. It is also desirable that one should be able to use one and the same method for all fuels.

The method proposed by M. Boerlage (*AB* ratio) would seem to fulfil all these conditions. It is noteworthy that with this method one can measure on the same motor with equal facility the octane number of fuels from 60 to 70.

At a time when the utilization of anti-knock fuels of high value is about to become current practice, we are very desirous that experiments of this method should be undertaken on a large scale in different countries, so that it might be adopted eventually as a universal standard test method.

2. *Materials Used.*

We agree with Mr. Banks' view that the exhaust collectors must all be of stainless steel, and although in the Air France Company we are still using some collectors made of ordinary steel, no new collectors are installed that are not of stainless steel.

The use of nickel–chromium steels with a low carbon content, 0·08 to

[*To face p.* 156.

UNIV. OF MICH.

0·15, gives good results, if a softening substance such as titanium is incorporated in it, and if the welding is correctly done.

But metallurgists are beginning to produce steels containing less than 0·08 per cent. of carbon, the fabrication of which should be easier than that of the previous materials, and the appearance, at least judging from the laboratory tests, should be equally good, perhaps even better.

We think that it would be interesting to encourage the metallurgists to continue along this line.

The use of stainless steels has made it possible to effect an appreciable reduction in the weight of collectors by the employment of steel plates

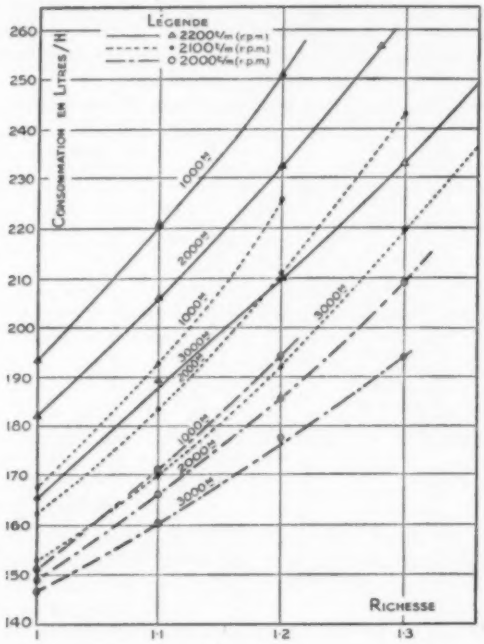



Fig. 3.

1 mm. or 8/10 thick in place of plates of 15/10, and to at least double the duration of operation without corrosion.

Inconel has also given good results.

With regard to sparking-plugs, we may say that, comparing the duration of operation, it leads us to conclude that one can allow 80 hours' operation between cleaning for plugs used with leaded fuel, whereas one can work a plug for 120 hours with unleaded fuel.

With regard to valves, we think that the use of supercharged engines very appreciably heats up the valves.

A study of the subject undertaken jointly by the Société Gnome and

Rhone and Air France has shown us the importance of cooling with sodium.

Sections were cut from valves taken from various sources, and by an examination under the microscope we have been able to show that the most fatigued part was situated about the middle of the curve joining the head of the valve to the stem.

Microscopic examinations of uncooled valves and of valves cooled with sodium have shown a very much better appearance of the latter.

3. *Consumption.*

At the beginning of the year 1936 we undertook a study of the fuel consumption during flight of Gnome and Rhone K. 14 motors, which has shown us that, especially on supercharged engines, it was of great interest to examine the consumption carefully, and that there were certain points of operation that were more interesting than others.

All the results and the curves obtained during these tests were published,

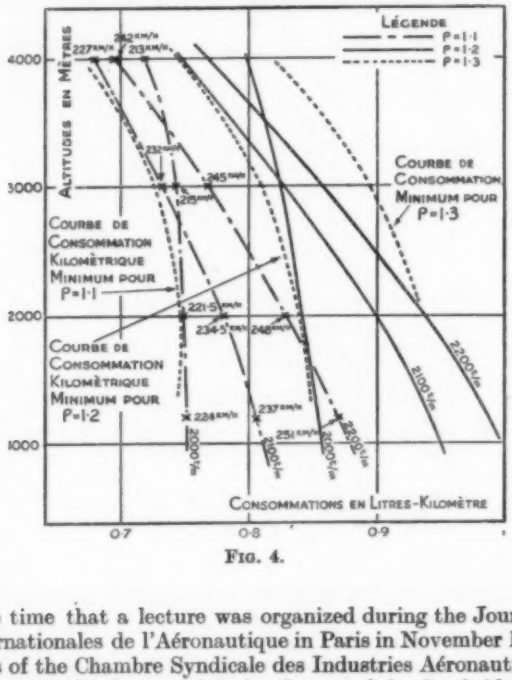



FIG. 4.

at the same time that a lecture was organized during the Journées Techniques Internationales de l'Aéronautique in Paris in November 1936, under the auspices of the Chambre Syndicale des Industries Aéronautiques.

It was shown in this lecture that, by the use of the Cambridge or a fuel-consumption meter, one could obtain appreciable economies, amounting to 25 and 30 per cent. in the most favourable conditions.

The three sets of curves given herewith show, on the one hand, the variation of the consumption of a K. 14 motor in flight with mixture strength, and, on the other hand, the variation of the consumption in litre-kilometres,

relative to altitude, the mixture strength and engine speed. Finally, the third graph shows the variation of consumption in litres, the altitude

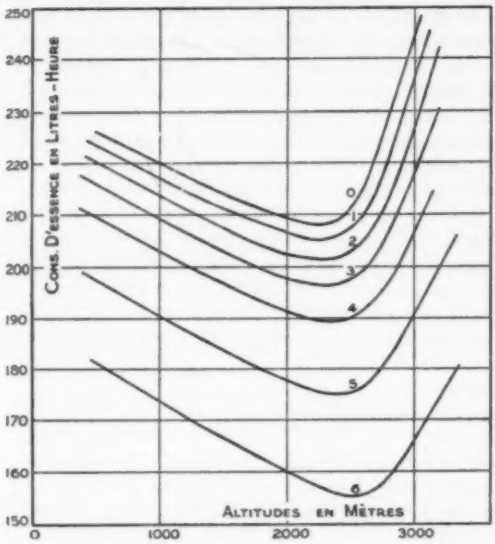



Fig. 5.

control being adjusted in a constant series of positions numbered from 0 to 6.

From Mr. A. R. Ogston :

Mr. Banks is to be congratulated on once more presenting a paper which is a most valuable contribution to the fuel problem, and which I feel sure will be used by many as the standard reference on this particular subject for some time to come.

However, if I may be permitted to make one very small criticism, it is that I consider Mr. Banks dismissed too summarily the question of the use of alcohol blended with gasoline in order to improve the performance of the latter in high-duty aero engines. Mr. Banks stated in the early part of his paper that the alcohols have not justified themselves as constituents of aviation fuel, a statement which is more or less true so far as the ethyl and methyl alcohols are concerned, but there are many other types of alcohol the uses of which as constituents of aviation fuel have so far not been thoroughly investigated, or, if they have, the results have yet to be made public. In my opinion, certain of the higher alcohols, such as *iso*-propyl, are likely to prove very valuable anti-detonants, and the remarks of Mr. Wood of Rolls-Royce, who informed us that his recent experiments had shown certain alcohol blends to display unusually good lead response, are, I submit, very significant. Incidentally, they confirm the suggestion

which I put forward to Mr. Banks in 1934 (*The Aeroplane*, 28.2.34) to the effect that the properties of tetraethyl-lead and alcohol could be usefully combined.

The utility of alcohol as an anti-detonant arises from both its very high spontaneous ignition temperature and its exceptionally high latent heat of vaporization; the latter property would largely overcome the difficulties which, as Mr. Banks pointed out, arise from the high boost temperatures created by superchargers and may even obviate the necessity for inter-coolers. Certain alcohols are also very efficient de-icers of the induction system.

I believe that one of the most suitable methods of utilizing the properties of alcohol will be by supplying it to the carburettor from a separate tank installed in the aircraft, rather than using a ready-mixed blend fed from the main fuel tanks; the separate alcohol feed could be controlled by the pilot, and probably need be used only when the engine has to be operated in excess of, say, 70 per cent. maximum power or during icing conditions. It is of interest to note that a special carburettor having provision for a separate and optional supply of alcohol was exhibited at the Paris Aero Exhibition a few months ago.

With regard to the question of the supply of whichever of the many types of alcohols is found to be the most suitable for mixing with aviation fuel, I think that it will be found that, once a demand is created, it will be producible in the United Kingdom in whatever quantities are required and at a price comparing very favourably with other high-octane materials the production of which seems at present to be a monopoly of the United States.

From Mr. A. H. R. Fedden:

The question of fuel correlation is most important, and although Mr. Banks shows that such excellent matching was obtained with the U.S. Army method in three different laboratories, it would be interesting to know if the fuels tested gave similar results under actual engine operating conditions of varying mixture strengths and temperature.

Indicators are mentioned, and particularly the cathode-ray type instrument. I regard the development of this of the greatest importance, and a form of indicator which allows measurement of the intensity of detonation is very badly needed.

Sparking-plugs are being pushed very hard with the present 87 octane engines, and intense development is necessary to meet the conditions for 100 octane fuel. Different materials may be necessary, and the Sinter-korund type needs careful investigation. The range of operation of engines is now so wide that the plug has to withstand a much greater range of heat flow, and it would be of interest to know if there is any information on the behaviour of plugs in flight on engines using 100 octane fuel.

Fuel injection, despite its many possible advantages, does not materialize, and the great amount of work put into the system in America appears now to have been cast aside. The system, apart from the engine functioning standpoint, might broaden the sources of available high knock rating fuels, owing to volatility being of lesser importance.

Fuel economy is of the greatest value, and, pending development of fully

automatic carburettors, exhaust gas analysers would seem to be very valuable instruments, in that the conditions of engine operation can definitely be controlled and the mixture strength adjusted to the best advantage.

Automatic ignition advance is mentioned. Variable ignition has undoubtedly an important bearing on engine operation, and is necessary in order to take advantage of the fuel both at take-off and for maximum economy under cruising conditions. Great demands are being made on the ignition apparatus, and considerable development is necessary in view of the constantly increasing speeds and pressures obtaining in the engine.

From Mr. F. R. F. Ramsay :

With reference to the remarks made by Mr. Banks on the subject of sparking-plug gap burning, I would like to present the following information for the consideration of those who are directly interested in this matter.

It has been proposed that magnetos generally give an excess of energy, and that, in the interest of plug-point erosion, this energy should be reduced, as it can be demonstrated that satisfactory ignition can be obtained with a very small amount of energy. However, the matter is rather complex, and the following is an attempt to state the problem clearly and to point out the dangers involved.

The magneto must give sufficient energy at a high voltage level to charge up the capacity in parallel with the gap to a voltage sufficient to ionize and break down the gap and permit a discharge to pass. The gap usually has resistance as well as capacity in parallel, due to imperfect insulation, chiefly in the form of deposits on the sparking-plug insulator.

Sufficient energy must be available to maintain the high voltage across this resistance until the gap ionizes and discharges the capacity. It is a fact that the energy required to charge a condenser to a given voltage is proportional to the square of the voltage. The energy dissipated through a resistance in a given time is also proportional to the square of the voltage. The energy required from the magneto, therefore, is proportional to the square of the voltage needed by the plug, and is directly proportional to the capacity in parallel with the plug (due chiefly to screening) and to the conductance (due to faulty insulation).

Examination of a spark in a rotating spark gap or mirror reveals that it consists of a single bright line, followed by a trail of flame interspersed with weaker bright lines. The first bright line is the very rapid discharge (of the order of 1 micro-second) of the capacity directly in parallel with the gap. It is generally conceded that this portion of the discharge accomplishes the ignition of the charge under normal conditions. The remainder of the discharge, which takes a relatively considerable time, and may contain the greater part of the total energy, is considered to assist in cold starting and in running with abnormal mixtures, but is otherwise useless. It tends to disappear when the parallel capacity is increased to near the point of misfiring, or when the gap is widened to increase the voltage to the same point. A small part of it is available as reserve energy for the first discharge, and the remainder consists of low-level energy which cannot rise to the voltage level required in extreme conditions.

Opinion is not settled as to the relative responsibility for point erosion

of the two portions of the discharge. However, an actual experiment may be quoted which shows that the capacity discharge may be chiefly responsible in spite of its short duration and smaller energy. In this experiment one set of plugs on an engine was fitted with 8 ft. 6 in. of shielded cable, with a capacity of about 350 micro-micro-farads, and another set of plugs on the engine was fitted with short plain cables of a capacity of about 10 micro-micro-farads. The plugs with plain cable ran five times as long as the plugs with shielded cable before adjustment of the gap was necessary. It should also be noted that the total energy of the spark through the shielded cable was slightly less than the total energy of the spark through the plain cable. The reason for the greater erosion of the capacity discharge lies in the very high rate at which the energy is discharged across the plug points.

The voltage required to produce a spark with a given plug varies widely with the running conditions of the engine. It is not uncommon for the voltage to vary from 3500 volts to 7000 volts in the course of a short run at various speeds. Four times the energy is required from the magneto when the voltage is doubled, and in order to satisfy this condition the magneto must continue to supply this amount of energy at the lower voltage as well. Plug erosion will cause the voltage to rise higher still, and a magneto output of eight times the energy required for normal running at full load (when the voltage is low) would be barely sufficient to meet normal requirements.

When the magneto is working at low voltage the excess energy is dissipated in the flame which forms the second portion of the discharge. At high voltage this energy is discharged in the capacity spark and the flame portion is reduced. If the results of the experiment quoted above are borne out, it follows that at low voltage the excess energy does not contribute greatly to plug erosion. The erosion of the electrodes due to the spark is largely determined by the voltage required by and the capacity in parallel with the plug. Any excess delivered by the magneto is dissipated in the flame following the discharge, without much effect on the erosion of the electrodes of the plug.

In further support of the contention that the capacity spark is mainly responsible for plug erosion under conditions where the capacity is considerable (as with shielded ignition), it should be noted that the rate of discharge of the capacity spark may be several hundred times the rate of discharge of the following flame. In actual fact, the capacity spark may be of the order of a kilowatt, while the flame may be of the order of a few watts.

Summing up the above, it may be seen that it is dangerous to reduce the energy of the magneto on the basis of the average energy required, since a small increase in voltage requires a considerable increase in energy. It also appears to be scarcely worth while to reduce the energy, since this will not greatly affect the erosion of the plug points, in the case of shielded ignition.

There has not been space to enlarge upon many interesting details of the behaviour of sparks which are relevant to the matter discussed, but these can be obtained by consulting the papers already published on the subject by various authorities.

From MR. B. H. MOERBEEK :

As regards the comparison of the U.S. Army Motor Method numbers with those of the C.F.R. Motor Method the writer is inclined to think that a misunderstanding has crept into the literature on the subject, owing to the fact that experiences with benzene were reckoned to hold good for other aromatics as well. Temperature measurements in a Ricardo E. 35, a C.F.R. motor, octane number determinations in a U.S. Army Method motor and tests in motors used in actual practice, some of the latter having been published, have convinced the writer that benzene occupies a very exceptional position as regards its effect on the temperature of the cylinder, for this temperature is higher than it should be according to the H.U.C.R. or octane number. Whereas benzene has a U.S. Army Method octane number that is much lower than its C.F.R. Motor Method octane number, because the U.S. Army Method determines the cylinder-head temperature as a measure for the anti-knock value, the U.S. Army Method octane number of toluene is higher than its C.F.R. Motor Method octane number.

In the U.S. Army Motor Method the effect of T.E.L. also corresponds more closely with actual practice than in the C.F.R. motor, especially if larger quantities are added.

Apart from the few minor points that I have dealt with above, I agreed with Mr. Banks' views, and greatly appreciated his interesting paper.

From MR. W. D. VAN OS :

During the past year the power output of the supercharged air-cooled radial engine has been increased considerably, and the horse-power output per litre of the different modern engines of this type in use on modern aircraft has been increased to approximately 30 horse-power at full throttle at critical altitude, and to approximately 35 horse-power during the over-boosted period allowed by the engine manufacturers during take-off.

This high power output per litre could be obtained not only by

*a.* experimental determination of the most suitable shape of the combustion chamber,

*b.* increase of the surface of the cooling fins of the cylinders and cylinder heads,

*c.* greatest possible effectiveness of the cooling of the engines, resulting from the most suitable installation, the application of pressure baffles and NACA-cowls with shutters, etc.,

*d.* increase of the turbulence of the gases in the cylinders,

*e.* use of fuels of ever-improved qualities,

*f.* design of special sparking plugs and experimental determination of the most suitable location of these plugs,

etc., etc.,

but also by the supply of an over-rich petrol mixture to the cylinders. The carburettors have been designed in such a way that the engines have a specific fuel consumption of 0·6–0·7 lb./h.p.hr. for the higher power outputs, whereas this consumption is not higher than 0·4–0·45 lb./h.p.hr. for operation under cruising conditions.

The method of using an over-rich petrol mixture is very effective.

However, according to the rare publications issued on the subject, we think it quite possible that injection of water into the inlet system of the engine—before or after the supercharger—can be even more effective.

We have some information from tests made on air-cooled aircraft cylinders, fitted on a single-cylinder testing machine, and following these tests it should be possible to increase the power output per litre by water injection easily by 10 to 20 per cent., without any inconvenience of abnormal high combustion pressures and cylinder temperatures.

We do not dispose of results obtained with tests on full-scale engines, and, so far as we know, no tests in this direction have been made on air-cooled radial engines. I think, however, that it would be worth while to investigate, by tests on full-scale engines, whether it would be possible to increase the take-off power of these engines considerably by means of water injection. We consider this especially of importance for engines installed in long-distance aeroplanes. The extra weight necessary for the installation does not need to be very great, as it is only necessary to have on board sufficient water for one take-off, and the installation need not be too complicated.

In my opinion water has not necessarily a prejudicial influence on the engines, assuming pure water will be used for this purpose.

We further see the possibility, if water injection takes place before the blower, that this increases the blower efficiency.

I shall appreciate very much Mr. Banks' opinion regarding the above-mentioned problems, and to hear whether he has any information concerning tests made in this direction.

From DR. W. H. HATFIELD:

With reference to exhaust pipes and collector rings, I would confirm that there are now available austenitic corrosion and heat-resisting steels which are sufficiently ductile as to render simpler the formation of the more difficult shapes required, particularly in collector rings, such steels having excellent resistance to oxidation up to a temperature of the order of 800–850° C., and at the same time being free from any susceptibility to intercrystalline corrosion either after welding or as a result of continued exposure to elevated temperatures under working conditions.

Another application involving somewhat higher working temperatures than exhaust pipes and collector rings is that where a portion of the exhaust system is included in a muff for air heating. Under such conditions of increased temperature where the 18 per cent. chromium 8 per cent. nickel steel, as usually supplied to D.T.D.171A, will not stand up, 'Immaculate 5' steel is suitable, this steel being capable of withstanding oxidation up to temperatures of the order of 1050–1100° C.

I was interested to read of the development of various types of inhibitor for use in petrol tanks made from some of the magnesium alloys. The use of austenitic non-corrodible steel for petrol tanks should obviate the necessity for such precaution and of course petrol tanks in such steel are in service.

MR. BANKS, in reply, said that owing to the short time available to deal with the points raised by the various speakers, he would reply fully to the discussion in writing. His written reply follows:

Before dealing with the main points of the discussion, I would like to thank the Chairman and Major Bulman for their very kind remarks regarding myself. I can assure them that these are much appreciated, and I would like to add that I have always had the greatest help from these gentlemen in their official capacity at the Air Ministry, and also from the other officials at the Ministry with whom I have come in contact. Without their help it would have been very difficult, if not impossible, to do my work efficiently.

Mr. Pye, Major Bulman and Mr. Thornycroft have all criticized the credit I have given to America for the part played by that country in fuel development. I wish to make it quite clear that I did not intend to deprive Ricardo of any of the credit which is certainly due to him for his work on fuels. At the same time, it must be remembered that Midgley and Boyd, in the States, were also responsible for some very valuable work on the development of fuel, and for giving us a specific material for the reduction, or elimination, of detonation.

What I intended to infer in my paper was that the Americans took advantage of the knowledge given to the world by these research workers (Ricardo, Midgley and Boyd) and applied it in a practical way long before anyone else.

Both Mr. Pye and Major Bulman have remarked on the fact that the fuel consumptions quoted by me in the paper are obtained from American sources, and that I have not mentioned the very promising figures already obtained in this country by the various engine builders.

I particularly stressed the American figures because these were obtained from already published data, and in some cases were also given to me quite freely by the aircraft operating companies in the U.S.A., and from other concerns in Europe who use American engines. So far, none of the data concerning the low fuel consumptions obtained on British engines have been published, and therefore it has not been possible to quote figures obtained in this country. I am very pleased to note that Major Bulman has given us a figure (0·38 lb. per b.h.p.hr.) which gives some indication of the fuel consumption which can be obtained on British engines using similar fuels.

As a matter of fact, it is my opinion that if we were as fortunately placed as America with regard to airline development, and with the mass of engines that country has in operation, our own motors would show up quite as well, if not better, so far as specific fuel consumption is concerned. I am aware of fuel consumptions obtained by British engines which, for a fuel of given anti-knock value, are superior to those obtained in America, and Wood [11] in his paper has given some indication of this.

Engines in this country are developed to use a fuel which has a somewhat lower anti-knock value than the fuels of similar octane number in the States. As mentioned in my paper, fuel to the D.T.D. 230 specification is rated at 87 octane, but due to the use of the modified Motor Method it is about two octane numbers less than a fuel similarly rated under Motor Method conditions.

By studying American and British data side by side, it appears that the mixture strength can be reduced to a greater extent in the case of our engines. It may be argued by those in the States that we have not the mass data in

this country to warrant the remarks I have just made, but we have considerable experimental data which show that British engines can be just as economical, and even more economical than those of their competitors when placed in similar service.

The foregoing remarks may appear to contradict those I have already made in the paper itself, where I have mentioned that American engines in general show a lower fuel consumption, but these statements compared modern American engines with present British types in airline service, and not with the experiments carried out on the latest engines in this country. It must be remembered that more than 90 per cent. of British engines are built to the order of the Air Ministry, and are operated under conditions which do not necessitate a particularly low fuel consumption, but until Major Bulman gave us some information on the latest developments in this country, it was not possible for me to embrace his comments.

I consider that American engine development in certain directions—that is, low speed (r.p.m.) operation at cruising power—is a very good method of obtaining low specific fuel consumption, but it is also my impression that such engines generally have to use a fuel of higher octane number than British engines for the same purpose.

I am very interested to have Major Bulman's remarks on the two-speed blower, and agree that, used along the lines mentioned by him, it should be regarded more as a definite development than an intermediate step, as indicated by me in the paper.

With regard to the flat engine, as Major Bulman rightly says, I do not regard it as entirely my own idea. In fact, I do not regard it as my idea at all, but mainly used the lay-out in order to show the centre-drive, from the crankshaft to the airscrew shaft, more clearly. In many cases the flat engine is not ideal, or even desirable, and, probably, would be of advantage only in the case of an air-frame of special or unconventional design.

In the case of the present, and what might be termed conventional, multi-engined aircraft of the low wing (or even high wing) monoplane type, the flat engine would probably have to be mounted ahead of the leading edge because, if placed in the wing proper, it would be difficult to arrange for sufficient fixed weight forward of the C.G. of the machine. The centre-drive arrangement, however, could be equally well used for the V or X types of in-line engines.

Major Bulman's closing remarks are also most interesting. In regard to drag, I am pleased to have his views on the future of the air-cooled engine, and it was due to a misprint that the word "radial" was omitted in the text of my paper. The comparison was between the radial engine and the liquid cooled in-line motor. I agree that the in-line air-cooled engine should be better than the radial for this purpose, but, if one goes to the in-line arrangement, is not the liquid-cooled engine better off from the point of view of length and compactness? I am seeking information on this rather than stating a fact.

I agree with Major Bulman on the question of getting the best from 87 octane fuel, in the way of engine development, before jumping to 100 octane fuel, but I think the Air Ministry very wise in issuing a provisional specification for the latter fuel, so that the engine-builders can have something to work on for their future developments.

I am most grateful to Mr. Thomas for the valuable information he has given on the questions of take-off power and thrust. Mr. Thomas is an authority on airscrews, and he has illustrated very clearly the limitations pertaining to large increases in take-off power.

To date, 100 octane fuel has been used in any real quantity only in America, and then only for engines which were originally developed on a fuel of 87 octane; consequently the over-all ratings of the engines concerned have not been increased, but the fuel has been used to permit a small increase in allowable boost for take-off, climb and operation between sea-level and rated altitude. One understands that this has been done by the military authorities in order to obtain experience with 100 octane fuel without delay.

From the information given by Mr. Thomas, and also from the investigations made along the same lines by Messrs. Rolls-Royce, I am in agreement with his last paragraph, where Mr. Thomas is of the opinion that, in order to make the best use of 100 octane fuel, the whole rating of the engine should be raised. As I have indicated in the paper, this will mean considerable development on the part of the engine-builders, so far as efficient supercharging, etc., is concerned.

I would like to thank Mr. Bass for his kind comments on the paper, and I am most interested in the information he gives concerning the tests carried out by the Delft Laboratory with sparking plug thermo-couples. I understand Delft has found that a thermo-couple embedded in the shell of the plug exposed in the combustion chamber gives more satisfactory results than one placed in the tip of the central electrode.

The remarks made by Mr. Bass concerning the influence of mixture strength on the relative knock ratings of fuels are also interesting.

I am in general agreement with Mr. Bass with regard to the effect of calorific value on fuel consumption, but recent work done by Messrs. Rolls-Royce appears to indicate that certain fuels, despite their lower calorific value, may allow a greater percentage reduction of mixture strength than that possible with other fuels of higher calorific value.

This has been found to be so in the case of "minimum fuel consumption" operation at reduced, or cruising, power, and comparison has been made between two fuels of 100 octane number, one being made up with *iso*octane and the other with *iso*propyl ether. In the case of the latter fuel it was found that the specific fuel consumption at reduced power could be decreased to a figure which more than compensated for the lower calorific value of this fuel.

Whilst no definite reason can be advanced for the behaviour of this fuel, it is probable that, although the two fuels in question were of the same knock rating, or octane number, the effective anti-knock value of the *iso*propyl ether blend was superior to that of the fuel made up with *iso*-octane, and the mixture strength could be further reduced on this account.

It seems, however, in the case of temperature sensitive fuels of low calorific value, such as ethyl and methyl alcohol, that whatever their knock rating they would not, and do not, show to the same advantage in respect of this lean mixture characteristic. Fuels composed of these alcohols generally demand a mixture strength which is on the "rich" side, and when adjusting the carburettors of engines to use such fuels it is

generally safe to calibrate the jet to give an increased flow which is proportionate to their lower calorific values.

Mr. Wood's remarks are very valuable indeed, and his Company is to be congratulated on the work it has done on fuels. In fact, Messrs. Rolls-Royce have contributed largely to our knowledge of the behaviour of high octane fuels in general.

It is interesting to note that, according to Mr. Wood's work, *iso*octane has, as he puts it, this "unfortunate weak mixture characteristic."

Another group of fuels, the ketones, which Messrs. Rolls-Royce have investigated, appear most promising, and show an extraordinary response to tetraethyl lead in relation to b.m.e.p. Technically, the ketones are very interesting indeed, and it remains to be seen whether these, *iso*octane or *iso*propyl ether, or a combination of them all, can be used to make up fuels of 100 octane and over.

The principal difficulty with all these fuels is the question of their supply, so far as both quantity and cost are concerned. Although cost may not be of primary importance, particularly for military use, production certainly is, both from the standpoint of military and of civil aviation; any blending agent which is chosen must be available in sufficient quantity.

With regard to the development of the high-duty engine generally, I have just received a copy of a very interesting paper * from America. The authors state that, as a result of their analysis, the most satisfactory method of employing high octane fuel is by a combination of high b.m.e.p. and high crankshaft speed. At the end of their paper there is a paragraph in which some important statements are made, and I am reproducing this paragraph herewith :—

> "An era of maximum pressure consciousness will be introduced during the next few years with improvements in pressure-measuring technique. The development must be pursued of pressure inhibitors (as distinct from detonation inhibitors) as effective as water but not requiring separate injection means. The cyclic variation in maximum pressure should be reduced, and we suggest as a means to that end that spark timing with spark plugs having electrodes with various degrees of electron emissivity be investigated. The thought occurs that, with the increase in mean effective pressures permissible with proposed fuels, an inevitable increase in engine speed will result and the problem of visualizing extremely high output engines becomes simpler as we accept the high-speed engine and properly weigh the design features as affected by pressures and speeds."

The opening part of the paragraph is of particular interest because Messrs. Rolls-Royce have already found, both in the case of fuels composed of *iso*propyl ether and the ketones, that the maximum cylinder pressures are reduced by at least 150–200 lb. per sq. in., at a compression ratio of 7·4/1 with boost, compared with 100 octane fuel composed of *iso*octane. Whether or not this is due to the fuels in question having a higher anti-knock value than their knock rating suggests is a matter for conjecture, and Messrs. Rolls-Royce wish to emphasize that these findings are the

* "High Output—And How," by R. N. DuBois and Val Cronstedt, presented at the Annual Meeting of the S.A.E. in Detroit, January 11th–15th, 1937.

result of preliminary work only, but they are investigating the matter further.

Mr. Dodds is to be praised for the work that he has done in the development of the cathode-ray indicator, and for the further applications he has found for this instrument.

There is little doubt that this type of indicator represents one of the most promising advances made, so far, towards the investigation of the behaviour of fuel in the engine cylinder. It is not yet entirely satisfactory for indicating the cylinder pressures of a high-duty aero engine, but this, I hope, will be only a matter of time.

It is, however, unfortunate that there is no truly reliable device for measuring cylinder pressures accurately, because it would be of particular value to obtain more data on the behaviour of the various fuels of high octane number which are now being tried in a practical manner by the aero-engine builders. It is also of particular concern to the engine designer to know the rate of change of pressure.

I am pleased to note that Mr. White has stressed the importance of availability in connection with the supply of these high-octane blending agents and fuels. At the moment everyone seems to be holding back and waiting events. That is to say, the fuel suppliers are awaiting demands from the engine-builders and aircraft operators for 100 octane fuel, and the latter wish to see what the fuel companies can really do in the way of production and cost before formulating any programme.

I wish to thank Mr. Thornycroft for his historical note on detonation, and also for the remarks he has made in regard to rotational swirl and turbulence.

This latter information is, in my opinion, most valuable, and until I had seen the swirl marks on the pistons in question I doubted very much whether swirl was a desirable thing to have in a petrol engine. Although the engine in question operates with a fairly good fuel consumption, I am of the opinion that it is inclined to be sensitive to detonation, but this may be due to the fact that it has large-bore cylinders and operates at comparatively low speed (r.p.m.).

I have since learned that the swirl marks are more or less accidental. That is to say, the engine-builders did not, apparently, develop the cylinder and induction system to promote swirl, but they are now investigating the whole matter.

I think, however, that the questions of swirl and turbulence are so bound up with cylinder head design, plug position, etc., that it is difficult to give a definite opinion; at least, until a considerable amount of further work has been done.

Mr. Beale's remarks are most interesting, particularly with regard to his views on the difficulties of applying the cathode-ray indicator to aero-engine cylinders. I hope, however, that he does not consider it a problem which cannot be solved because the prize, in the matter of knowledge gained, will be so great if the indicator can be successfully applied.

Regarding the last two paragraphs of Mr. Beale's contribution, and concerning the method of detecting detonation which is now being developed at Sunbury, I should be interested to know if he considers such an instrument, or method, suitable for aero-engine cylinders, or whether it is more applicable to rating fuels on the standard knock testing unit.

It is thought that, under conditions of incipient detonation, the increase in pressure may not be large, and one wonders whether this method, applied to a full-scale engine, would be sufficiently sensitive; since it is known that inaudible or incipient detonation can initiate accumulative heat troubles in the case of an aero-engine cylinder.

Mr. Coxon's remarks are pertinent, and although I agree with him that there are many problems to solve, such as a method of properly rating 100 octane fuel, and also its supply in adequate quantity, I cannot but feel that this is all in the day's work and it is the price we must pay for progress.

There are two ways of looking at any new development, so far as its practical application is concerned: a positive way and a negative way. The positive way, which must always involve some risk, is to go ahead and produce the material, whatever it may be, so long as the eventual users want it enough to pay a reasonable price commensurate with the advantages it offers. The negative attitude is to say that the material is difficult and expensive to produce and why change anyhow, when what we have is "good enough?"

In research and technical development it is rarely the case that anything is "good enough."

So far as the 100 octane fuel situation is concerned, it reminds me of a well-known advertisement for babies' rusks which, in so many words, says that if you want anything badly enough—scream for it. I feel that if those concerned in the progress of aviation consider that this fuel is worth having, they should follow the advice of the advertisement in question.

I think that the home-defence squadrons of the R.A.F. should be provided with equipment to take advantage of 100 octane fuel, because this country is literally the nerve-centre of the Empire; and even if the supply of such a fuel were limited, the use of high-duty equipment might prove decisive, in the air, in the early stages of a war. In any case, the European nations are not likely to be any better off, and when the supplies of this fuel have been exhausted, we will all be on the same basis and have to de-rate the engines, in boost and compression ratio (not a big job), to use fuels of inferior knock rating.

Regarding the last paragraph of Mr. Coxon's contribution, I do not think that it would be advantageous to develop engines to use fuel having an octane number below, say, 87, because we would then be at a disadvantage respecting the performance of our aircraft, both military and civil, as compared with other nations that have been using 87 octane fuel for some time.

I am not quite clear as to the meaning of the latter part of the paragraph, where Mr. Coxon mentions "solid injection." If he means the C.I. engine, then, from a military point of view, this does not at the moment offer any advantages, and the supply of fuel for this type will present just as many difficulties in time of war as will the supply of an aviation petrol which can be leaded up to a reasonable octane number; because both will probably have to be imported.

So far as petrol injection is concerned, this system should not greatly alter the situation where high octane fuels are concerned.

Mr. Pomeroy has evidently not read my paper very carefully. In the

first place, I have specifically mentioned that I am discussing only those fuels of 87 octane and higher. It appears to me a retrograde step to develop engines on low octane number fuels, at least lower than 87, when this fuel is offered and is available in adequate quantity.

Whatever is done along the lines suggested by Mr. Pomeroy, how much more can be achieved with a fuel of higher octane number? The change from the old D.T.D. 134 (Air Ministry) specification to the present one, D.T.D. 230, has been responsible for an increase in the order of (approx.) 40 per cent. in the rated power of British engines. The octane number range represented by these two specifications was from (approx.) 74 octane to 87 octane, respectively.

Regarding exhaust valve temperature, here again Mr. Pomeroy has obviously scanned the paper rather than read it, because on page 75, par. 6, I have particularly stressed the importance of cooling the combustion chamber, valves and sparking-plugs. Again, on page 81, par. 3, I have advocated the use of the fully cooled exhaust valve. No one likes a hot running valve, but it must be remembered that engineering in all its phases is a matter for compromise, and it is not always possible to have everything as one would like it.

Concerning the last paragraph of Mr. Pomeroy's contribution and the high m.e.p. obtained with relatively low octane fuel mentioned by him, I am aware that the rotary valve in question is the most promising so far produced, but it has yet to prove itself so far as the large-bore high-duty engine is concerned. I am doubtful if it can show an advantage in cost and mechanical application, relative to the sleeve valve, to which I have also referred in my paper.

Further, although the figures mentioned are certainly impressive, I am concerned only with supercharged engines where the use of high, or higher, octane fuels will usually result in beneficial increases in power due to the increase in boost and compression ratio permitted.

I am most grateful to Mr. Meyer and his Company for the trouble he has taken, firstly, to come from Holland for my lecture and, secondly, for preparing a valuable contribution to the discussion. This contribution is all the more valuable because the K.L.M. may be considered as one of the most progressive air-line operators in the world, and certainly in Europe. Its equipment is always up-to-date, and therefore provides great opportunities of obtaining data for the improvement of engines and aircraft, which must reflect favourably on operating efficiency and passenger comfort.

I am interested in Mr. Meyer's remarks concerning high-altitude operation and the possible use of lower octane number fuels, but I am inclined to the view that it will be more satisfactory to employ the same fuel for flight cruising as for take-off. There are experimental data to show that it is possible to obtain a larger reduction in fuel consumption, by being able to reduce the mixture strength to a greater extent, with high octane fuel than with one of lower value.

Also, when cruising at the altitude mentioned (25,000–30,000 ft.), and having in mind that engines will be supercharged to restore their rated or cruising power at around these altitudes, will it be advisable to reduce the anti-knock value of the fuel? There is a relatively long period

to consider, where the machine will be climbing to gain altitude, and also the reduction in air density with increasing altitude may affect the cooling of the motors.

I agree with Mr. Meyer that lubrication is a most important matter in connection with the modern aero engine, and as the specific duty is increased it is becoming more difficult to obtain satisfactory operational periods between overhaul. No sooner does the airline operator work up the operating period to, say, 400–500 and even 600 hours, when a new engine type is produced of higher performance which, until considerable service experience is obtained with it, must be limited to about 350 hours' operation.

I am not qualified to say much about lubrication, and would prefer to leave it to others who are more intimately concerned with this question.

I would add, however, that engines, particularly for airline service, may develop along lines suggested by the latest Wright "Cyclone" G-100 engine, which has apparently been produced specifically for this purpose. This engine has a high performance, but will be operated at a conservative rating. The take-off power is about 1200 b.h.p. but, it is stated, only 1000 b.h.p. will be used in service, with a cruising power of about 550 b.h.p. The engine has a bigger diameter than its predecessors, due to increased cylinder finning, and I believe it has longer-skirted pistons. It is designed to use 100 octane fuel and is reported to have a consumption of 0·43 lb. per b.h.p.hr. at cruising power.

I wish to thank Dr. Underwood for his remarks concerning the materials mentioned by Mr. Wood, and agree that these are most promising technically. It remains to be seen whether it will be possible, or rather feasible, to produce them in any real quantity.

In answer to Mr. Millar concerning the exhaust turbo-supercharger, I think the fuel consumption should be better with this type than with the mechanically driven blower, but I have no data to offer in support of my views. The only turbo-blower in general service at the moment is that developed by the U.S. Army Air Corps and the General Electric Company, which is fitted to the "Conqueror" engine installed in the "Consolidated" P 30 fighter. I understand that this engine has a reasonably good fuel consumption, but since the engine itself is of somewhat out-of-date design, it might not be fair to compare it with modern liquid-cooled engines, having mechanically driven blowers, and which are giving relatively low fuel consumptions compared with this particular job.

I am also particularly grateful to Mr. Ploix, and Air France, for his attendance at my meeting. I also wish to thank him for the valuable data in his contribution, which are obviously the result of a considerable amount of investigation.

I am interested to have Mr. Ploix's remarks on the question of assessing the anti-knock value of fuel, and agree that perhaps some method similar to the "AB ratio" proposed by Mr. Boerlage may be suitable for rating fuels accurately in relation to their performance in full-scale engines. I think, however, that a considerable amount of work will have to be done before a test method can be evolved, and it is going to complicate matters considerably if the oil companies have to use a supercharged fuel test unit for the testing and rating of fuels in the laboratory. However, there may

be little alternative but to accept the situation if such a method gives the desired results.

Finally, I again wish to thank Mr. Ploix and Air France for the other valuable data with regard to fuel consumption in flight, and also the remarks he makes concerning the materials used for the construction of exhaust rings, and for the photomicrographs of the exhaust valves. This information is a valuable addition to my paper.

I wish to thank Mr. Ogston for the kind remarks he has made with regard to my paper. I think I made it clear in the paper, when mentioning that the alcohols have not justified themselves for aviation purposes, that it was the ethyl and methyl alcohols to which I mainly referred. Actually Mr. Wood, in his contribution to the discussion, referred to " alcohol derivatives," and has since stated that these are the ketones.

Mr. Ogston mentions one very important property of the lower alcohols—that is, their exceptionally high latent heat of vaporization. However, the higher alcohols do not possess this advantage, although their latent heat is somewhat higher than that of ordinary petrol. I have dealt in detail with the disadvantages of ethyl and methyl alcohol, and it is my experience that these two alcohols in high-duty engines are liable to give rise to pre-ignition, and consequently serious damage to the engine. They appear sensitive to temperature and insensitive, or rather unresponsive, to additions of tetraethyl lead. The higher alcohols, such as *iso*propyl, are probably better in this respect, but do not seem to offer any particular advantages relative to the other blending agents, such as *iso*octane, *iso*propyl ether and the ketones.

The ordinary alcohols, ethyl and methyl, are certainly useful for carburettor de-icing purposes, but the latest technique in this direction appears to be that of designing a carburettor which, in itself, does not ice-up under appropriate conditions. I am, however, aware of carburettors which, in addition to their ordinary functions, employ alcohol for de-icing purposes.

I am grateful to Mr. Fedden for his contribution, and with regard to his first paragraph, I would say that I only gave the results in question in order to illustrate the high degree of reproducibility it is possible to obtain with the U.S. Army Method. It has yet to be proved that this method can be modified to rate high octane fuels accurately in relation to their performance in full-scale engines, but it appears to me that a test method along these lines may be more satisfactory for rating these fuels than the present C.F.R. Motor Method procedure.

I am also glad to note that Mr. Fedden is in agreement with me so far as the development of a suitable indicator is concerned.

Mr. Fedden's further remarks on the question of sparking-plugs, fuel injection, fuel economy and automatic ignition advance, are worthy of close attention by those who are concerned with engine development.

I am indebted to Mr. Ramsay for the information he has given on the subject of ignition. It has been my experience that those concerned with aero-engine development have been inclined to disregard the " mechanism " of ignition, and often such items as the sparking-plugs, the ignition cables, and magnetos appear to be fitted to the engine in a rather haphazard manner.

The almost universal use of radio, necessitating the screening of plugs

and cables to avoid radio interference, and the employment of high octane number fuels, has made it necessary to give the ignition system of the engine serious consideration and attention. Mr. Ramsay's contribution, therefore, is all the more valuable because it serves to focus the attention of those concerned with the proper functioning of the modern high duty engine, on a vital point.

Since presenting my paper I have been asked whether "Sinterkorund," as an insulating material for sparking-plugs, will actually prevent or reduce deposit build-up on the insulator, resulting from the use of leaded fuel. So far as our investigations in this country have gone, it appears that a Sinterkorund plug can suffer just as much in this respect as one having a mica insulator, but in the former case the Sinterkorund is unharmed by the deposit. However, when the deposit attaches itself to the insulator surface it can also cause electrical breakdown in the case of the Sinterkorund plug, but when we know how to use this material to the best advantage, it may be possible to produce a plug which will not suffer from deposit accumulation to the same extent as the present types of mica plug.

So far as mica plugs are concerned, it has been ascertained that corona has a detrimental effect on engine performance. Whilst the presence of corona has been known for some years, in the case of mica plugs, it is only relatively recently that it has been found to have an important effect so far as engine operation is concerned. To those who are not familiar with electrical ignition the explanation of corona is as follows: It is a leakage of current within the mica insulation and paralleling the central electrode of the sparking-plug, and is visible through the mica. The presence of corona is detrimental to the functioning of the sparking-plug and effects the spark at the plug points proper.

Mr. Moerbeek has made some interesting observations in regard to the comparison of ratings obtained by the U.S. Army Method and the C.F.R. Motor Method. I am pleased to have his remarks concerning the behaviour of benzene. I believe that the U.S. Army Method was evolved purposely to de-rate benzene to a certain extent in relation to gasolines, or petrols, of the straight-run variety, because at that time benzole was similarly de-rated in full-scale American aero engines. It was appreciated by Heron that fuels containing a fairly high proportion of benzole were characterized by the way in which they caused a rise in cylinder head temperature at, or near, detonating conditions. I believe also that, due to this feature, the temperature-plug method of rating fuels was evolved and the bouncing pin discarded.

Whilst I have not the paper by me at the moment, I believe Klein [13] in his latest work obtained very good results with toluene blends. I also wish to thank Mr. Moerbeek for his kind remarks concerning my paper.

In reply to Dr. Hatfield, I am pleased to have his remarks concerning exhaust-pipes and collector-ring materials. In connection with any exhaust system, it is most important, in my opinion, to design it so that it does not run at excessive temperatures. Until recently it has always been my impression that the exhaust system of an engine has been regarded as an afterthought by the engine-builders, whereas it is really a most important part of the engine, particularly the air-cooled variety. It can

have a large influence on the cooling of the cylinder head and the stressing of the head locally to the exhaust port.

The piping and manifolding comprising the exhaust ring should be of round or oval section, and it should not have any flat sections, which are a fruitful cause of splitting, due to fatigue caused by vibration and heat. This is particularly the case if the stub pipes from the cylinders to the main exhaust ring are arranged so that the gases impinge directly on to the ring material. In other words, it is better to lead the pipes into the ring so that the gas is discharged at an angle or tangentially to the ring surfaces.

In regard to the latter paragraph of Dr. Hatfield's contribution, I am aware that there are some petrol tanks made from non-corrodible steel in experimental service, but these are by no means in general use. In connection with these steel tanks, I would be interested to have some idea of their weight, for a given form of tank, in relation to those made of aluminium and magnesium alloys.

The remarks made by Mr. Van Os are most interesting and instructive. I am in general agreement with his analysis of the technique which has enabled the engine-builders to obtain increased specific power output; with the possible exception of item (*d*), which appears questionable. This point is covered by Mr. Thornycroft in his contribution to the discussion, and my reply to him.

Regarding the question of water injection, I suggested this scheme, which I do not claim to be original, about a year or so ago, but, so far as I am aware, little has been done in the matter.

Water is a very valuable inhibitor of detonation. What is almost more important is its inhibiting effect on excessive maximum cylinder pressures. It would certainly be valuable in reducing boost or charge temperature.

What little has been done with water injection appears to indicate that a fairly large quantity is necessary for this purpose, amounting to about 30–50 per cent of the fuel consumption. Whether or not water injection will have a detrimental effect on the engine is a matter for conjecture, but it is known that, when used in early types of heavy oil engine, its continued employment caused considerable cylinder and ring wear.

In view of what has been stated by Mr. Thomas and others, regarding take-off power, I am wondering whether the use of water will be worth further consideration, because it appears that high boost pressures, for take-off purposes, may not be required and that high engine speeds (r.p.m.) are more desirable.

Since completing my reply to the main discussion I have received a letter from Mr. Arthur Nutt, of the Wright Aeronautical Corporation, in which he criticizes some of the statements I have made in the paper. Mr. Nutt, who is an authority on aero-engine matters, scarcely needs any introduction by me to those concerned with aviation in any of its aspects, and I consider that, in fairness to the air-cooled engine-builders, his remarks should receive publicity, and I have his permission to quote the principal of these herewith :—

"On page 105 you refer to Young's paper in which 0·34 lb. fuel consumption was obtained. I agree with you that this figure is unusually low and, frankly, was produced under rather ideal conditions which are not

easily reproduced. However, I do not think that your conclusions are correct that the engine would not operate continuously at this figure. We do not see any reason for difficulty if no detonation is present and the cylinder temperatures are as low as they are in actual operation.

"You refer to the automatic mixture control for carburettors. This device is not automatic unless the temperature of the mixture is held constant, but does correct for pressure up to the critical altitude of the engine, at which point it is no longer automatic. Recent developments indicate the use of fully automatic carburettors for both temperature and pressure which should be in service this year.

"I also note your statement regarding American engines running at lower piston and crankshaft-speeds than similar British types. This is true in the case of the Bristol engine which does run at appreciably higher piston speeds, but it is interesting to note that the 'Kestrel' and the 'Cyclone' are running at almost exactly the same piston speed.

"From our standpoint, we have kept our engine speeds as low as possible, in the interests of low fuel consumption and reduction in reversals of stress, but as time goes on you will notice that engine speeds in this country are increasing particularly for take-off. We are raising our take-off speeds on the 'Cyclone' to as high as 2400 r.p.m. and Pratt and Whitney are, I understand, going as high as 2600 r.p.m. on the 'Twin-Wasp.' I see no reason why we cannot increase our engine speeds satisfactorily still further when it is needed in spite of the one pound valves which we are using.

"Regarding your flat engine, it makes an interesting picture primarily because it has no accessories or supercharger. If the supercharger is mounted on the rear of this engine I am sure that you will find it very much larger in diameter than would be ideal as far as a flat engine is concerned. Of course, the depth will not be as great by any means as a radial engine, but the value of the engine as a flat engine would be greatly reduced because of the necessity of having considerable diameter in the supercharger. I am not sold on the use of flat engines because it is not definitely determined as yet that the engine mounted inside of the wing will be any better as far as aeroplane speed is concerned than the engine mounted in the conventional manner. Skin friction may be an important factor, but the fairing of the propeller and propulsive efficiency must also be considered.

"You also bring up the matter of the amount of power available in single-row engines. Many people thought that a 500-h.p. engine was the limit of a single-row aircraft engine. Now you have elected to prophesy that 1000 h.p. is the new figure. We are selling Cyclone engines for domestic consumption at 1100 h.p. take-off and, as I have repeatedly said, the power is going up, and we know no reason why it should not continue. We have actually pulled 1220 h.p. from the 'Cyclone' engine on the dynamometer indicating the possibilities for take-off power with 95 octane fuel with this engine for some time in the future. We have not exhausted the higher speed possibilities in this engine which will permit us to run with the same m.e.p., and therefore the engine should not be more 'fuel sensitive' than it is at the present time. We have no evidence to support the fact that the 'Cyclone' is any more 'fuel sensitive' than our small 14-cylinder engine. These two engines are about the same displacement per minute, and the 'Cyclone' is doing a lot better job in the way of power

output. In defence of the two-row job I do not believe that the air from the front cylinders in any way affects the cooling of the rear cylinders. Our experience has been that the rear cylinders generally run cooler than the front cylinders, probably because the air has a better chance to reach the rear cylinders because of the longer time to straighten out and flow through the baffles properly."

Referring to Mr. Nutt's first paragraph, I still feel that it would be difficult at the moment, for the engine concerned to operate continuously at the fuel consumption quoted.

I am glad to have his remarks concerning automatic mixture control for carburettors, and also regarding the questions of piston speed and r.p.m.

In reply to Mr. Nutt on the flat engine, I would refer to my reply to Major Bulman, but I think, so far as the supercharger and other accessories are concerned, these could be mounted on the lower part of the crankcase with the supercharger in a horizontal plane.

Mr. Nutt's closing paragraphs concerning "fuel sensitivity" are most interesting; I still hold that the big bore low-speed engine is inclined to be sensitive in this respect, and the fact that the "Cyclone" engine mentioned by Mr. Nutt is employing a fuel of 95 octane (C.F.R. Motor Method), approx. 100 Army Method, would indicate this; since other engines of about the same total cylinder capacity, but having a larger number of smaller cylinders, appear to be giving similar take-off power on 87 octane (C.F.R. Motor Method) fuel. This does not detract in any way from the recognized excellence of the "Cyclone" engine, although its restriction to a 100 octane fuel for the power in question is an important consideration.

# ORGANIZATION OF RESEARCH IN THE PETROLEUM INDUSTRY.

By Ir. J. H. Vermeulen.

SYNOPSIS.

The paper deals with the organization of the physical, chemical and related mechanical research work in a Central Research Laboratory in the Petroleum Industry.

It is held that such research work should be carried out *centrally*, and that, besides research work, there is a great deal of Service (Routine) work to be done. The principal conditions (position, sources of information, scientific contact and contact with the world of practical application) for the satisfactory functioning of a laboratory of the kind are described.

A form of organization (with the work divided into Routine and Ordinary Applied Research on the one hand and Pioneering Applied Research and Pure Research on the other) is indicated in which, in the author's opinion, the conditions described have the best chance of success.

The paper concludes with remarks on Reporting and Supervision.

## Introduction.

Of recent years quite extensive literature has been published on research —that is, both on the concept " research " and on the different types of research. It is clear from this literature that neither the definition nor the classification of research has been given very objectively, but that both bear a very subjective outlook.

If, like Boyd, one defines research as consisting principally " in searching for new knowledge or in trying to improve something," it is evident that in the petroleum industry all kinds of research work are carried out in practically all its branches, *i.e.* in the oilfields, the refineries with their auxiliary branches, and in distribution. It is, however, necessary, and is, indeed, gradually becoming customary, to speak of research within more defined limits, and to interpret it as consisting in carrying out those experiments in the fields of geology, physics, chemistry and mechanics by which new methods of investigation are developed or applied, or which lead to the preparation of new products, or the devising of new methods or new applications.

This paper will limit the term research still further, and will deal mainly with the *organization of the physical, the chemical and the related mechanical research work in a central Research Laboratory of a petroleum company.**

This research does extend, however, to the various phases of the

* The literature cited in the reference is concerned principally with the more theoretical side of the concept research, with the subdivision according to types of research and the related definitions and examples, while moreover arguments are advanced in it in favour of the great utility and necessity of research work of all kinds. For this reason the author of the present paper considers himself absolved from the necessity of entering further into these aspects of the problem.

petroleum industry. Thus the Research Laboratory is required to solve problems in connection with the exploration and exploitation of the oil-fields, such as the colloido-chemical investigation into the flow of mud flushes (reduction of viscosity), work on the plastering of oil-sands, examination of oil-well cements and the quest for new demulsification agents.

For storage and transportation of crude oil and gas the Research Laboratory will be called upon to study corrosion and flow problems and to investigate evaporation losses.

Undoubtedly the main task of the Research Laboratory is to deal with the work required to refine the crude oil into marketable products, which includes the necessary investigations to develop fresh applications for existing products; or, conversely, to adapt the products obtained in the petroleum industry to existing applications. Examples of groups of investigations belonging to refining problems are: Work connected with distillation, condensation, cracking, extraction, hydrogenation, chemical refining, polymerization, etc., while the groups of investigations on applications of petroleum products include the improvement of the resistance of lubricating oil to oxidation, the development of good extreme pressure lubricants, the manufacture of good aviation spirit, the improvement of the properties of asphaltic bitumens or bituminous emulsions to be used for road-making, flooring, the manufacture of roofing material, bituminous paper and coatings.

## Why a Central Laboratory?

In a petroleum company with world-wide interests *decentralization* is unavoidable. The oilfields and refineries are widely scattered; this fact and the regional diversity of the nature of the applications and specifications for them make decentralization the natural form of petroleum industry.

Yet the need will be felt for *one central body* in which the technical and scientific problems may be studied and *guidance given*. It will therefore be necessary for the directorate to such a large industry to secure technical and scientific *advice*, for which laboratory work is very often essential.

It would be inadvisable to decentralize this laboratory work—that is to say, to carry it out in the localities where the difficulties occur, or where new methods are applied. The various problems would then be dealt with too specifically, and a solution might be sought exclusively of the local difficulties. The results of this local investigation would not be available for the solution of similar problems in kindred branches, and there would be no gain on the theoretical side of the general problem. Moreover, decentralized industrial laboratories would be very uneconomical: they would entail the duplication of buildings, equipment, etc. It would also be difficult to find the necessary number of various types of research chemists.

The advice is primarily destined for the management, and therefore, in a certain sense, this is the authority issuing the orders. It will make its wishes and intentions clearer by personal contact. All these motives point to the conclusion that a Central Laboratory is the indicated form of organization.

If such a Central Laboratory is regarded as the place whence advice is to be given on a number of technical and scientific problems concerning the industry, it will be evident that such advice may sometimes be obtained by simple routine work. In many other cases it can only be given after more or less extensive research work. It is evident, therefore, that in a Central Laboratory a great deal of routine work will be done alongside research work, and is undoubtedly necessary to create an organization in which not only all the necessary facilities for research shall exist, but in which normal work shall not suffer in any way.*

*What are the Conditions under which such a Laboratory can Function Satisfactorily?*

The ideal position for such a laboratory would be: near the centres of production, the refineries and, if possible, the centre of an important application—such as automotive and aviation industry—and near the body to which the reports have generally to be submitted, hence near the Head Office of the company. It is rarely possible to fulfil all these conditions, and as contact with the Head Office is certainly regarded as the most important factor, the Central Laboratory is usually built in the neighbourhood of the Head office. It may be found to be highly conducive to the efficiency of the Central Laboratory if one or more of the other requirements can be fulfilled at the same time.

*Information.*

The more isolated the position of the laboratory with respect to the various phases of the industry, the greater the likelihood that the advantages of a centralized—and therefore more general—view of certain problems will be lost. The result might be that the particulars necessary to get a grasp of a scientific or technical problem are more difficult to obtain. The author wishes to stress the fact that these difficulties should not be under-estimated.

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* The author uses the following terms to distinguish two kinds of research: *Service Research* and *Pure Research*.

By Service Research is understood that laboratory research work, the immediate objective of which is to achieve direct, practical results. This definition approximately corresponds to that for "Applied Research" in Stine's paper, and to the description of an industrial research chemist's work in Dunstan's paper.

This service research work includes a quantity of work which, although research work—*i.e.*, laboratory work for which the method of investigation cannot be defined in advance—is a kind of research work which has few general aspects, is incidental and has the character of service in a marked degree, while in the course of the investigation it is often influenced by changed circumstances or changed views of those who have ordered the work. This is called "*Short-time Service Research*," and may be compared with what is called "Ordinary Applied Research" in Stine's paper, in contradistinction to the "Pioneering Applied Research" (Stine) or "*Long-time Service Research*."

The latter is of a more general character, and is less dependent on incidental, varying views and circumstances. As an example of "Ordinary Applied Research" may be mentioned the investigation into the suitability of certain base materials for the preparation of a synthetic lubricating oil, if at least the "Pioneering Applied Research" subject: "The preparation of synthetic lubricating oil by polymerization of olefines" has already been worked out completely as a process.

That research work which is carried out to deepen the knowledge of the nature of the physical or chemical processes which are of interest may be termed "*Fundamental Research*."

In his opinion, in a big, decentralized petroleum company it is essential to provide for a special organization to meet such difficulties.

The purpose of this organization is to collect the various technical, scientific and also commercial data, or those pertaining to patents, and make them accessible in a convenient and systematic form. These particulars will have to relate to the production, refining and applications. To these last, in particular, commercial particulars are indispensable. Therefore, general technical and commercial documentation may prove of great service to other functionaries besides the Central Laboratory. Preferably this organization should be housed, not in the Central Laboratory itself, but in the Head Office. However, the various data are useful to the *laboratory* only if they are sufficiently detailed and scientifically docketed. A functionary who is fully conversant with the chemical and physical work of the Central Laboratory should be quite familiar with that documentation.

*Keeping in touch with Practice.*

Every research centre is faced with certain difficulties. The research work, chiefly the pioneering applied research, may become too remote from the desires and needs of refining and industrial practice. To avoid this it is very necessary that contact should be established between the research workers and the various works or the customers using the commercial products.

An opportunity of following the course of processes worked out in the laboratory when they are applied on a full scale by refinery or customers, is an excellent means of promoting the practical orientation of the scientific staff. Such an opportunity should always be provided, both by the "technical documentation" referred to above, and by personal contact.

Intimate, direct contact between laboratory staff and customers is certainly essential; widening the prospects for applications of oil products will undoubtedly contribute towards increasing profits. Only regular and personal contact with the technical staff at the customers' works can lead to the most efficient adaptation of products to new applications.

*Scientific Contact.*

Conversely, opportunity must be afforded the research workers of keeping abreast of new scientific methods and new theories. To ensure this they must, besides studying all the important articles and books on their subject, keep in touch with the Universities, visit congresses and be in contact with colleagues engaged in kindred and other industries.

*Routine Research.*

As already stated, a considerable amount of routine work will be done in this Central Laboratory alongside of the research work. Therefore, provision should be made for the undisturbed progress of the research work while the routine work is being dealt with promptly and efficiently. It is not enough to admit this in theory; a form of organization should be chosen which ensures its practical application. The same applies to the variations of the research work, viz. applied research and

pure research. Care must be taken to avoid the tempo of pure research work being retarded by the applied research work, and vice versa.

Let it be well understood that the author does not mean to imply that there shall be no inter-relationship between the routine work, the applied research and the pure research; on the contrary, it is highly desirable that there should be some interplay.

*Staff.*

The question of staff is without doubt the most essential factor governing the proper functioning of the research laboratory. It is merely mentioned here; for further particulars reference may be made to Dunstan's paper,[1] which deals very fully with the training and type of laboratory staff.

It is obvious that the qualifications of the scientific staff of a Central Laboratory vary with the different functions and the types of laboratory work. When dealing with the various types of work, these requirements will also be further discussed.

*Working Conditions.*

It goes without saying that there is a large class of conditions which may be summarized as "Organization conditions for the proper functioning of the laboratory apparatus," such as :—

Good scientific documentation with a well-furnished and arranged library, effective and prompt circulation of periodicals and abstracting of such, and filing founded on a technical and scientific basis.

Very efficient dealing with samples to be examined is necessary. The availability of a comprehensive collection of representative samples, catalogued on a technical basis and provided with technical and analytical data, representing the various phases of the industry or connected with various applications. Last, but not least, there should be well-equipped laboratories with auxiliary services such as departments for the construction, repair and testing of equipment, control of chemicals, etc.

## What is the Best Form of Organization for a Central Laboratory?

It will be clear that a laboratory of this kind is very extensive, and varies greatly in the type of investigations that have to be carried out. There is, then, no escape from the fact that this laboratory must itself be decentralized into various Departments. The first question to arise is: According to what principle must this division into departments be realized?

This may be as follows :—

(*a*) Division according to the nature of the *products* that have to be examined or refined; *e.g.* oil investigations (to be further subdivided into, say, light products, gas oil, lubricating oil, etc.), bitumen, and gas investigations, etc.

(*b*) Division according to the nature of the *operations current in the working of the petroleum industry*, such as distillation, extraction, crystallization, cracking, hydrogenation, polymerization, chemical refining.

(*c*) Division according to the nature of the *laboratory methods*, thus

distinguishing between a physical, colloido-chemical, electro-chemical, organic, and analytical department, etc.

(*d*) Division into Departments in accordance with the classification: Routine work and Research work.

It would be wrong to give preference to any one of these divisions. Experience has shown that each of these types of division, either as main division (Department) or as subdivision (Sub-department), has special advantages for certain investigations or at a given moment and may therefore then be utilized.

However, to make the research work in the Central Laboratory answer its purpose most effectively, it is advisable to make a functional division into:

A. Routine work and Ordinary Applied Research on the one hand, and

B. Pioneering Applied Research and Pure Research on the other.

For, if the utmost is to be got out of research work, it is very necessary that it should be done in an atmosphere of quiet and concentration. If the results of the experimental work are such that the investigation threatens to come to a standstill, there must be an opportunity for study and reflection so that at least the possibility of new lines of departure may be opened.

If, in the same department, service work has to be done which calls for quick handling, entails much correspondence and involves the holding of discussion, it is only comprehensible and human for those concerned to turn away from the difficult, now somewhat stagnant investigation and to direct their attention and energy to the mostly very urgent, shorter investigations. It is obvious that attention is thereby deflected from the research subject far longer than it should be, and that the time for study and reflection has been wanting.

Then again, those working in these two groups of investigation should have quite different qualities: Type A workers must be perfectly familiar with the wishes and demands of those from whom they have their orders, and with the form in which the reports should be drawn up. They must generally try to adapt themselves as far as possible to the widely fluctuating purposes of their investigations. They must also, to the best of their ability, familiarize themselves with the technical aspects of the problems; while last, but not least, they must have administrative talent and a pronounced sense of co-operation.

Type B, on the other hand, must primarily have great experimental talent, and must take delight in absorbing himself in the details of the various subjects. The research staff must possess not only great gifts of scientific leadership and initiative, but must also have a sense of the value of their work for practical purposes.

It will be evident that these two different combinations of qualities are rarely represented in one person.

*Division of Section A.*

It is further advisable to subdivide Section A into departments which are partly arranged according to laboratory methods, and partly to the nature of the products.

Certainly, the most important departments among them are the *analytical departments*, such as the analytical oil department (analyses of crude oil, gasoline, kerosine, lubricating oil, fuel oil, paraffin wax, vaseline, lubricating oil, greases, emulsified oils, etc.), the analytical bitumen department (analyses of bitumens and bituminous mixtures), the gas-analytical department. These three divisions are made both according to the nature of the products and to the differences between the analytical methods.

*Refining Departments.*

A number of departments, also belonging to Section A, are the non-analytical departments which act as consulting departments for refining problems. Their task is to solve all questions connected with the refining of crude oil along various lines up to different final products. According to the extent of the work, it may be further subdivided as to products.

*Application Departments.*

Then, difficulties will constantly be cropping up with practical applications and with distribution and, if the extent of the market of the product in question permits, it will be necessary to create separate service departments in group A to deal with simple complaints and difficulties arising in the sale or application of the products, if these problems are outside the scope of the analytical departments. As a rule, chemical and physical tests will not be exclusively used in these application departments, but more technical and mechanical methods will be needed. As examples may be mentioned : departments for the application of asphaltic bitumen and emulsion for road-making, for paper-making, etc.

A department of the kind is certainly justified for the application of lubricating oil, and it is easy to understand that physical or chemical laboratory work, alone, certainly will not suffice to solve problems raised by complaints of this product from customers. Often those problems will have to be solved with the aid of engine tests, for which a separate Engine Department is essential. It is, therefore, desirable that lubricating-oil difficulties should be solved by means of physical, chemical and mechanical investigation, and with the utmost possible co-operation.

*Division of Section B.*

As soon as one gets to the subdivision of *Section B* (section of Pioneering Applied Research and Pure Research), it will be found that subdivision according to *departments*—which are usually looked upon as more or less permanent departments with a fixed range of investigations—is less felicitous.

The most ideal subdivision is that which is as flexible as possible, and which enables the Management to place a certain group of research investigations in the hands of a number of chemists and/or physicists who are judged to have the best qualifications for that particular type of work. For each of these cells a suitable chemist or physicist should be designated to take charge (Cell System, see Boyd, p. 47).

As a rule, it will be best to keep the cells small, and the number of investigations entrusted to them will also have to be as small as possible

(about two to three), and careful watch will have to be kept to maintain proper balance between staff allocations and nature, number and extent of the investigations as they proceed.

This may be done by leaving the staff of the cell intact and directing appropriate investigations to them. An alternative is to group the *investigations* into cells and, whenever the nature of the investigations makes this necessary, to vary the number and special type of chemists and physicists concerned.

Thus in the former case one has the grouping of *staff*; in the second, the grouping of *problems*.

Unless special circumstances make it impossible, preference will as a rule be given to the former procedure, since mutual understanding and the gift of good leadership are undoubtedly essential conditions for the success of the investigations. Once these conditions have been established in a given cell, one should not disturb them unnecessarily.

Now, by what guiding principle should one combine problems and staff?

There can be no fixed rules for this. The choice of the members of the staff will be governed by such considerations as their experience, training or special branch of study (physics, physico-chemistry, colloido-chemistry, organic chemistry, etc.), their aptitude for building apparatus and for reporting. This complex of qualities decides the type of work with which to entrust them.

When grouping problems one will, as far as possible, combine analogous subjects, such, for instance, as extreme pressure lubricants and the oiliness of lubricating oil. There may also be cells studying certain operations. Thus, a polymerization cell may be formed which deals with the whole range of polymerization, hence irrespective of base material or final product. Similar cells are a hydrogenation cell, a cracking cell, an extraction cell, a cell studying the problem of separation by crystallization, etc.

There is a great advantage in combining a number of these cells and putting a senior chemist or physicist in charge, so that the whole research is under the supervision of a research staff of three or four directing officers who, of course, must keep very closely in touch with each other.

In some cells, in the case of certain problems, physical, chemical and mechanical research are intimately connected by the nature of the problem. In that case the closest contact should be kept between the various workers.

*Routine Work of the Cell.*

A question needing further consideration is whether the *routine work*, which is always intimately connected with research work, should be carried out in the cell itself or allocated to the routine department of Section A. As a general rule, work should not be given to other departments if it entails the risk of slowing down the speed of the service work done for outside bodies. Moreover, very often the interpretation of the routine figures can be carried out more profitably by the research workers themselves, who know exactly for what purpose and to what degree of accuracy the various analytical and other particulars are required. If testing equipment has not yet been completed or fully adapted to the type of problem, such work will certainly have to be done in the cell itself. Only

when very special experience or very special equipment is necessary for the work, which is of the normal routine type, the routine departments of Section A will be the right place to do the work. Thus one will certainly not have C.F.R. or H.U.C.R. tests made in a research cell engaged on the manufacturing of aviation spirit. There would be no advantage in giving up the accumulated experience of fractionating and distilling in the distillation department for the sake of assisting some research work. Nevertheless, in these cases it will sometimes be advisable to transfer one of the workers in the research cell temporarily to one of the departments of the routine section to do the work which is required for the research in question under supervision of an expert.

*Auxiliary Service.*

This cell-formation may even be applied to some auxiliary services, especially when making equipment in the Instruments Department and the Glass Blowing Department.

There is a tendency to attach one or more glass-blowers or instrument-makers to a cell, preferably in or adjacent to the locality where the cell is working. These people then adapt themselves exclusively to the needs of that particular cell and become absorbed in that particular work. Such an auxiliary service to a cell inevitably grows to a complete instrument-making or glass-blowing department in which all types of work have to be carried out, but where it is not possible to make efficient use of the equipment.

The indicated course is to keep the Instruments and Glass-blowing Departments centralized, at most in different rooms, one for Section A and one for Section B, and then to group the employees in the latter according to cells or cell combinations.

*Pure Research.*

How does Pure Research link up with this section B?

As a rule the various subjects of Pure Research will originate in the difficulties and unsolved problems that come to light in Pioneering Applied Research, and which cannot be further dealt with there, because that would entail too radical a departure from the original objective. It then becomes the task of Pure Research to carry out those investigations which are calculated to deepen knowledge of the essentials of the particular problems, so that Pioneering Applied Research may later reap the benefit of that increased knowledge.

The form which the organization may assume will be one of the two following: One may either have a separate Pure Research Department in which several cells are formed for specific groups of investigations; or one may attach one or more Pure Research workers to a cell or cell combination of Section B. The advantage of the latter form is that the pure research workers participate very intimately in the work of the pioneering applied research people, but it involves the danger of their drifting too far from their own objective, and themselves becoming really applied chemists or physicists.

Theoretically it is, of course, quite correct that the results and views obtained by pure research experiments (generally made with pure chemical

compounds with simplified reaction schemes) should be available before starting on pioneering applied research, which is applied to highly complicated base materials met with in the petroleum industry.

Practice, however, requires the exact contrary. It will invariably be necessary, owing to the needs of refineries or applications, to tackle the problem in a practical way without yet possessing sufficient knowledge of the theoretical side of the matter. If the importance of the problem warrants it, it will be wise research policy to have the purely theoretical side taken in hand while the practical aspect is being dealt with, either in the same cell, or in a separate department.

*Semi-technical Department.*

Semi-technical installations in which laboratory results can be applied or worked out are indispensable to a research laboratory.

The semi-technical operations which can be combined with, or are the result of, investigations classified under Group A will be such as can be carried out with standard equipment and in accordance with standard processes. The staff of the semi-technical department will not have much difficulty in linking their work to that of the laboratories of Section A, and will be able to do it fairly independently.

It is a different matter with the semi-technical work resulting from the Pioneering Applied Research of Section B. Sometimes, however, this research work cannot be carried out in a laboratory only, because the dimensions and running of the equipment are not convenient for such a locality, and also, the whole method may still be unknown and the equipment itself not yet been developed. In this case, the work in the semi-technical department should be regarded merely as an extension of the work of the various cells in the laboratory. The semi-technical staff, however, will not be able to carry it out; the work will have to remain in the hands of the workers in the cells, or, if necessary, somebody will have to be appointed who has the right semi-technical feeling and experience ("Semi-technical B cells").

If the result of the work in these "semi-technical B cells" is such as to warrant really trying out the process in a pilot plant, the time has certainly arrived for the staff of the semi-technical department to take over the work from the B-cell workers and to put the process into operation.

*Liaison between Sections A and B.*

Special provision must be made for the interchange of experience and views between Sections A and B, and it is also necessary that the results of the Pioneering Applied Research, interpreted in a practical way, shall come to the notice of the Directorate. Someone with wide experience of refinery and general practice, who must have a clear grasp of the developments which the research offers and the customers' want, will be needed to provide for correlation between Sections A and B and a correct interpretation of the results of Section B.

It will certainly not be possible to realize this link as the function of one individual; it will undoubtedly be necessary to split up this work according to products, such as oil, bitumen, etc.

## Reporting and Supervising.

Finally, a few words on two important questions, that of reporting and that of supervising, chiefly concerning the work of Section B.

*Reporting.*

In this research work a great quantity of data come in during the experiments which are at first unarranged, while neither ideas nor the lines of further investigation will have assumed definite form. Too precipitate, intermediate reporting to outsiders might certainly be harmful, and, indeed, is generally rightly opposed by the research workers.

Nevertheless, it is highly desirable that the particulars collected from the very beginning should take some definite shape, and thus emerge from the chrysalis stage of rough notes and note-books. To this end a kind of "experiments documentation" should be instituted, which means that from the very beginning a report is made on the activities of the research staff and their assistants in connection with a given investigation or part of it.

This "documentation" shows in a concise form, but as far as possible chronologically, what investigations have been carried out, what figures have been obtained and with what apparatus—possibly with a description and drawing of that apparatus—the experiments have been carried out. This documentation, which is posted up weekly, must, however, remain strictly domestic, "domestic" meaning that these data are perused and criticized by the manager of the cell in question and, maybe, by one of the senior chemists of the research staff.

This experiments documentation must constitute the basis for the intermediate, summarized reports which the managers of the cells are to write. This intermediate and final reporting on the work done in the cells may perhaps best be called "experiments *reporting*." It will be evident that it is unnecessary for the various date to be reported on *in extenso* here, but that what is required is a clear, conveniently arranged *résumé* of the results obtained, with pertinent conclusions and an indication of the suggested further procedure. This reporting is nevertheless fairly detailed, intended for the research staff and the link between Sections A and B, and *externally* only for those who should be placed in the possession of *details* to enable them to put into practical effect the new or improved processes or applications described in reports.

Besides this form of reporting, there is another which is highly desirable. This may be called "Directorate Reporting," and is destined for the directorate of the Central Laboratory and for certain directing bodies of the head office. The distinguishing mark of this form of report is that it is brief and readily surveyable, omitting all unnecessary details, and clearly indicating the purpose of the investigation, the way this was carried out, and the results and conclusions reached from the work. It is decidedly unnecessary for the cell staff to write these reports themselves. It is far better to have this done by reporting chemists and physicists specially appointed for the work. Their work should not be under-estimated; they must be good stylists, must be fully conversant with the investigations with which they are dealing, and must have a well-developed feeling for the

essential part of the work, and stress what it is most important for the managing directors to know.

*Supervision.*

In concluding with some remarks on supervision, it should be understood that it is the *general* supervision of such a laboratory which is meant, and not the special scientific research management, which, naturally, is in the hands of the research staff and the "links."

The general organization, besides having the care of the general management, will also be concerned with the following problems :—

*Section A.* Service tempo; manner in which the wishes of those who bring the problems forward are to be fulfilled; decision as to how the various departments and sub-departments are to be staffed for the work to be done; checking and, if necessary, amending the task of the technical and administrative auxiliary services.

A complex of administrative rules regarding registration of problems, administrative control of procedure, reporting and correspondence on the problems, handling samples, use and acquisition of equipment and chemicals is indispensable and, if applied with discretion, greatly enhances the efficiency of the work of Section A.

*Section B—Pioneering Applied Research.* For this part of the laboratory work general supervision and control are also necessary, even though it will naturally be more flexible than for Section A.

The primary task will be the formation of the cells, both as to grouping of staff and to that of the problem.

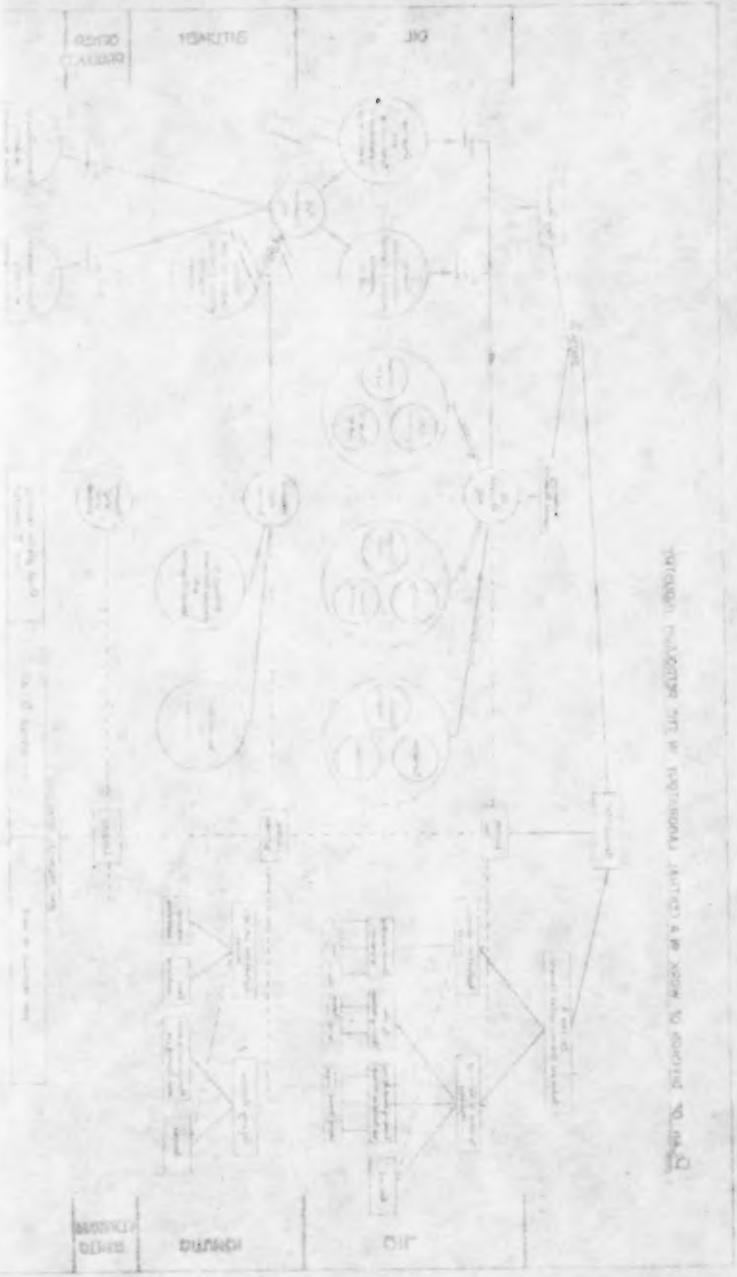
Registration of problems will also be necessary for this section, though control will be concerned far less with tempo and service than with the proper way of solving the problem and timely reporting. General rules and control pertaining to the experiments documentation (reporting) and reporting to the Management described in an earlier part will certainly have a *raison d'être.* Equally useful are rules relating to literature and patent searching.

*Section B—Pure Research.* The greatest possible liberty should be allowed and the least possible amount of administrative regulations made for this work. The choice of the subjects, however, should be made in consultation with the Pioneering Applied Research staff and the Management. The extent of each investigation in itself may be limited more or less by the allowed budget. If necessary at all, the registration of subjects should be made in very general terms. Reports should be issued mainly when interesting results have been obtained. There is, moreover, an incentive to reporting as soon as these research workers are allowed a certain freedom to publish in scientific periodicals.

## Conclusions.

It will have emerged from the foregoing that the author regards well-founded organization with a functional division into Routine and Research as necessary. A complex of administrative and other regulations will promote the efficiency of Routine and Ordinary Applied Research Work.

It is desirable that the Pioneering Applied Research should have more



PLAN OF DIVISION OF WORK IN A CENTRAL LABORATORY IN THE PETROLEUM INDUSTRY.

[To face p. 191.

liberty, while the Pure Research should be restricted as little as possible by rules and regulations.

General technical and managerial supervision of the organization and progress of the research is much to be desired.

Yet all these various possibilities can become effective only if a sound, business-like spirit prevails amongst the laboratory staff themselves, coupled with the desire to co-operate, even to the extent of sinking personal views, so that in this way the research work may be most efficient to the Company.

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# RESEARCH AND DEVELOPMENT ACTIVITIES IN THE STANDARD OIL COMPANY (NEW JERSEY) INTERESTS.

By W. C. Asbury and David A. Shepard.

A study of the principles governing the organization of research in the petroleum industry may be approached logically in either of two ways:

(1) From the fundamental principles of organization generally, or,
(2) From an outline of an existing organization in that field, as an example of the practical working of the governing principles.

The ultimate difference in the results given by these two methods of approach may be slight, since an existing organization will naturally be based upon the abstract principles involved, and, conversely, the abstract principles will essentially have reference to, and be based upon, the working of a concrete organization and its development.

In this paper a description of such a concrete organization is considered with the thought that an exposition of the structure will make clear the principles governing its form, and the comments here are, therefore, necessarily limited to one organization in the petroleum industry on which data are given in considerable detail.

Since its incorporation, sixty-five years ago, the Standard Oil Co. (N.J.) has been engaged continuously in research and development. This has not been purely a matter of foresight—it has been an absolute necessity in an industry which has been required to solve new chemical and engineering problems on an unprecedented scale while endeavouring to keep up with a rapidly expanding and shifting market.

The development of new processes and products has proceeded at such an accelerated rate in recent years as to excite interest in the manner in which the necessary inventive activity is stimulated and directed. How this is effected within the confines of the Standard Oil Co. (N.J.) interests is discussed in this paper.

It should first be explained that the Standard Oil Co. (N.J.) is a holding company only, and is the parent company for several hundred wholly or partly owned subsidiaries and affiliates. As such, its position is that of an owner, as distinguished from that of an operator. All of its production, transportation, manufacturing and marketing operations are carried out by subsidiary and affiliated operating companies.

The territory which research and development activities must cover is obviously as diversified as the interests of all these operating units. To meet these diverse needs, a technical organization has grown up which combines centralization and decentralization. The problems peculiar to

each major operating unit are studied in laboratories owned and operated by that organization. In addition, however, all of these operating companies are served by a commonly-controlled central staff organization—the Standard Oil Development Co. Formed originally as a patent holding company for the service of the operating units, it now operates research and development laboratories, carries out engineering and testing work, and co-ordinates the scientific and technical as well as the patent activities of the operating units. In addition, it has some special commercial activities which are the outgrowth of its technical and patent business. More pioneering research is carried out by the Development Co. than by any of the operating units, and much service work is also done for affiliated operating companies which do not maintain complete laboratory and engineering organizations of their own.

Of the group engaged in carrying on technical activities, some 60 per cent. are occupied largely by control and design problems; the remaining 40 per cent. can be considered to be engaged in various phases of research and development work.

In the Standard Oil Development Co. the principal laboratory units at present are those at Bayway, N.J., fifteen miles from New York City. Here are the Esso Laboratories, employed in research directed to the development of new processes and products and to the evaluation of the latter. The extensive motor laboratories of this unit are provided with equipment suitable for testing fuels and lubricants in motors ranging from the smallest one-cylinder stationary unit to the biggest diesel-powered truck. In temperature-controlled engine and chassis testing rooms the conditions of arctic winter or tropic summer may be duplicated with equal facility. To speed up work many engines are put through definite operating cycles by automatic controls. Elaborate equipment is in use for studying combustion. Special test machinery is available for investigating lubrication under extreme pressure conditions, for determining oiliness, for testing greases in various bearings, auto springs and shackles, gears, etc.

In the chemical division of the Esso Laboratories a variety of highly specialized apparatus is in use for determining the oxidation resistance of fuels and lubricants. Here many special products are also evaluated such as textile oils, ink oils, paraffin wax, launching greases, leather oils, ball bearing greases, cutting compounds, steam cylinder oils, etc. The utilization of refinery by-products is a major objective of the Esso Laboratories.

Another group at Bayway is engaged in studying refinery processes. The laboratories of this Process Department are fitted up largely with semi-plant equipment suitable for carrying out studies of cracking, distillation, solvent extraction, dewaxing and other refinery operations. Refinery processes and petroleum stocks are evaluated, often with particular reference to finding the optimum conditions for operation. About half of the work is of a service nature on problems raised by the various refineries, and the remainder is mainly on process development and research. The more or less routine demands incident to service work help to maintain a close contact with refinery needs and indicate the avenues which research may follow most profitably.

The General Engineering Department is also located at Bayway. Com-

plete refineries, storage plants and equipment of all sorts: stills, furnaces, fractionating towers, power plants, storage tanks, etc., are designed by this organization. In addition, a corps of engineering inspectors is maintained to make periodic safety inspections of the more hazardous types of refinery equipment. Construction materials of all sorts are purchased on specifications drawn by the Materials Division, and are inspected by General Engineering representatives at the suppliers' plants or on delivery. Extensive metallurgical studies are conducted to ascertain the best materials for use at high or low temperatures, under corrosive conditions, etc.

As an intermediary between the Process and General Engineering Departments a Process Engineering Department makes process surveys, conducts plant tests on old and new processes, investigates new refinery methods introduced to the industry, and in general covers the field between the research man in the laboratory and the engineer in the drafting room. In this function the Department has the particular responsibility of guiding research through economic studies of process requirements.

On a smaller scale the product-testing activities of the Esso Laboratories are duplicated by the recently organized Esso European Laboratories. These laboratories devote their attention largely to matters of product quality arising in Europe. Esso European Laboratories, located in London, are, like their more extensive counterpart in the United States, well equipped for chemical and internal-combustion engine studies. Stationary and automotive engines of gasoline and diesel types are available for fuel and lubricant investigations. Two controlled-temperature rooms, one of which is believed to be unique in Europe in that it is provided with a chassis dynamometer, make possible the testing of engines or complete chassis under conditions simulating any atmospheric temperature normally encountered in Europe.

European refinery problems are handled in major part by laboratories directly associated with each refinery, such units having been set up at the Port Jerome and La Mailleraye works in France; at Teleajen, Rumania; Fawley, England; Trieste, Italy; Vallo, Norway; Libusza, Poland; and Harburg, Germany. Occasionally the larger American laboratories are called upon for direct advice; more often data already accumulated by the exchange of reports between all technical centres in the Jersey interests supply the needed information.

Returning to North America, attention should be called to the large laboratories maintained by the operating companies at Baton Rouge, La., Baytown, Texas, and Sarnia, Canada. The activities of the Baton Rouge laboratories are turned largely to the development of new processes, and it is here that most of the oil hydrogenation developments have been made.

The Baytown and Sarnia laboratories are concerned mainly with specific problems of their operating Companies, the Humble and Imperial Oil Cos. respectively. Both have, however, contributed much to general interest problems. Baytown has been particularly active in the polymerization field and also has a large group of specialists engaged in problems of research on oil production and geophysics. Sarnia has contributed extensively to the knowledge of dewaxing and asphalt manufacture and use and to the development of the phenol extraction process.

The laboratories of Stanco Inc. at Bayway study such products as Nujol, Flit, and other oil specialties.

A step removed from the true development picture are the Standard Inspection Laboratories, a unit of the Development Co. This group is engaged in testing products in their main laboratory located at Bayonne, N.J. Representatives or correspondents at the other American refineries check up on refinery shipments to see that all meet specifications. The Standard Inspection Laboratories serve also as a referee between the various operating units in all questions pertaining to products quality. This organization has been active in standardizing test procedures ever since its organization in 1880, or thereabouts, by George M. Saybolt, inventor of the Saybolt viscometer, chromometer, and many other petroleum testing devices in less general use. At present these laboratories are actively working with the C.F.R. on octane number testing standardization and regularly supply secondary octane number reference standards to the industry.

Close contact with marketing requirements is maintained through the Sales Engineering Department, a unit maintained by the Esso Marketers. This technical organization as the result of its promotional activities and constant study of customer requirements, is especially able to recognize the possibilities of outlets for new products and need for improvements in existing ones. This unit also oversees the introduction of newly-developed products to the field.

Ever since its organization it has been the practice of the Standard Oil Development Co. to support programmes of research in special fields in university laboratories wherever a situation arose in which this policy could be advantageously applied. Such programmes are usually under way in several different university laboratories. The experience of the Development Co. with this type of work has been a very happy one. The constructive results from this policy may be summarized briefly as follows:

In the first instance very successful solutions of certain types of research problems have been obtained by turning these problems over to outstanding specialists in the academic world, giving them adequate funds, facilities and assistants. In many cases the assistants engaged by these independent scientists for the prosecution of the research programmes in the university laboratories have been men of outstanding ability who through their contacts with the Company on these programmes have been brought into the organization as permanent members. A more indefinite but perhaps equally important result of this policy of supporting research by outstanding specialists in the academic field has been the stimulus which the close working contacts thus created have given to the men of our own personnel.

The activities of all the technical staffs are followed closely by the Patent Department of the Development Co. Most of the inventions of Jersey employees are assigned to the Standard Oil Development Co., and every effort is made to induce men to submit their ideas promptly. The original idea, in memorandum form, is passed for comment to those department heads most familiar with the subject-matter, and action is subsequently taken in line with their recommendations. The handling of the memoranda, as well as the preparation and prosecution of any subsequent patent

applications, is assigned to patent attorneys each of whom is a specialist in a particular field.

In this work the Patent Department is greatly assisted by the Technical Library at Bayway, which carries some 6000 technical texts and bulletins on its shelves, together with files of 300 publications. The Official Patent Journals of all countries which make abridgements available are reviewed, and some 40–50 patents per week are singled out for special attention. Over 100,000 patents have already received such study. This Technical Library serves all of the technical staff and laboratories.

A fundamental principle in the direction of the research and development programme of the Jersey interests has been the recognition of the importance of the contributions to petroleum technology made by independent scientists and technologists. A fixed rule which is binding upon every responsible technical executive of the Jersey interests is that he must keep an open mind on the potential value of the work of the independent technologist. As a result of this policy there have been developed many mutually advantageous affiliations by the S.O.N.J. interests with individuals and groups, both inside and outside their own industry in relation to new inventions and scientific advances.

# THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE One Hundred and Seventy-third General Meeting of the Institution was held at the Royal Society of Arts, John Street, Adelphi, on Tuesday, December 8th, 1936, Dr. DUNSTAN occupying the Chair.

The following papers were read and discussed :

## ORGANIZATION OF RESEARCH IN THE PETROLEUM INDUSTRY.

By Ir. J. H. VERMEULEN.

## RESEARCH AND DEVELOPMENT ACTIVITIES IN THE STANDARD OIL COMPANY (NEW JERSEY) INTERESTS.

By W. C. ASBURY and DAVID A. SHEPARD.

### *DISCUSSION.*

THE CHAIRMAN said he was perhaps in an unique position in having known intimately both laboratories of which the lecturers had spoken, and he could vouch for the extraordinarily good and most effective work that had been carried out in those two great organizations. He was a little disposed, however, to contemplate with misgiving Mr. Vermeulen's chart, which laid down in rather closely divided cells the operations of the various individuals concerned in so-called research. He used the word " so-called research " purposely, because, after all, there was Research with a capital R and research with a small r, and it seemed to him that one was rather inclined to confuse those two aspects. He was inclined to think that the actual research man—the man who was concerned with the development, with the invention, with the propagation of new ideas—must be, as he was sure Mr. Vermeulen would agree, as completely unfettered as possible : once such a man was tied up into any kind of stringent organization his utility was to a large extent diminished. He could call to mind in his own organization—and, after all, he had been concerned for twenty-odd years in industrial research—a man who could not possibly be placed into any kind of cell, who would escape from the cell, and yet who was a man of really astonishing inventive and research capacity. Any research scheme must provide some sort of way in which people of intensely vigorous inventive capacity could be allowed to develop in their own way. One could, of course, imagine a sort of laboratory in which such men were locked up for, say, three months, and instructed to produce a new idea, as a hen laid an egg; but if the industry did not provide some way in which that particular type of brain could function, then he submitted that the industry would be losing a great deal of research activity which could be and ought to be of the greatest benefit. Briefly he pleaded for freedom in development.

He was sure that members had listened with immense interest to the two

most instructive papers. Anybody who had had the chance of seeing the laboratories in Amsterdam and Bayway could bear witness to their great efficiency. Some few weeks ago he had visited the Bayway station and looked over the whole place, and had been very interested at the way it was run. It did give the individual the maximum opportunity of working out his own scientific salvation, and he was sure that Mr. Shepard would agree with him that that was an ideal generally to be followed. It was the same in Holland, as those members of the Institution would remember in our visit a short time ago. He would particularly commend to their attention the views expressed by Mr. Boerlage on that occasion.

PROFESSOR JOCELYN THORPE said he believed it was Mr. Skimpin who was asked to open a case, and when he had opened it found mighty little in it. He saw himself in a similar position; he had very little to talk about in this case, because Mr. Vermeulen and Mr. Shepard had said all that he had to say, and he congratulated Mr. Vermeulen on having brought before the Institution a scheme of research which was altogether admirable. It was now nearly eight years ago that he had had the pleasure to visit Elizabeth and see the Standard Oil Company's laboratories. That was, of course, in the days before Lead tetra-ethyl, and since then very great advances had been made.

As Mr. Vermeulen had said, research in industry must definitely be of two kinds; and when the speaker said "industry," he included the petroleum industry, because, after all, there was not much difference between industrial research, as it should be done, in all the various industries which needed research.

The first he would call research work of the *ad hoc* type—that is to say, the works laboratory in which there was a constant interchange between the refinery and the laboratory for the solution of problems arising during works practice. That kind of laboratory was absolutely essential, and it was one which should form the centre of a great deal of industrial activity.

The other kind of laboratory should be devoted to what he called long-distance research. The speaker knew there was a feeling that long-distance research ought to be carried out by the universities, and Mr. Shepard had mentioned this in connection with the organization in vogue in the Standard Oil Co. of New Jersey. This is true up to a point, but nowadays, when industry is becoming more and more a part of pure knowledge, the universities themselves, unless they are in close touch with what is going on in the factories or in the industries, cannot give that directing assistance which they would wish to give. In the long-distance laboratory a research worker would, however, be in close touch with the universities, not only in connection with long-distance research, but also in the provision of personnel. It must not be forgotten that it is from the university laboratories that the personnel for the laboratories must come—and it is the duty of the universities to see that the men who will ultimately take prominent positions in industry, are men who are thoroughly trained in the fundamental principles of the science underlying the industry they wish to enter. Not only should there be a close interchange and intercourse between this kind of laboratory and the universities, but there should also be a very close connection between the *ad hoc* laboratory and the laboratory for long-

distance research. In the works there will occur frequently practical problems which cannot be solved immediately, and which have no real apparent technical importance, but which require to be investigated in the long-distance laboratory, and these would then automatically pass from the *ad hoc* laboratory to the laboratories of long-distance research.

The speaker did not altogether agree with the Chairman that the Research workers were necessarily beings apart. He personally had come across some of them; they did exist, but they were very rare—the man in blinkers, for instance, who could only see just a little bit ahead of him, and concentrated all his vision and his brain on following what he could see in front of him. He occasionally came across that type, and they must, of course, be "given their heads" entirely, otherwise they would do nothing; but the average man that they turned out, for example, from South Kensington was a man of ordinary ability, thoroughly grounded (he hoped) in the fundamentals of his science, and one who would adapt himself by reason of his knowledge to any process that might be put in front of him. The speaker did not believe that it was necessary to do more than merely put a thoroughly trained mind in front of a machine, and such a mind should be able to grasp its purpose in a very short time, provided always that he had a sufficient knowledge of engineering to enable him to follow an engineer's description. However, he might be wrong on that point; but still, that was a point of view which he held very strongly, and he believed it to be one which others held with him.

The research of a fundamental character which would be carried out in the long-distance research laboratory would be such as should have no immediate commercial bearing; and when he said "no immediate commercial bearing," he meant, naturally, that one could not say that if the research failed it would affect the industry to any great extent. He would be inclined so to arrange matters that the student placed in that laboratory would not only have a free run of the distillery or of the factory, but would also be in close touch with the common room. Those people should not be segregated, to his mind: they should be in close touch with their fellow-workers in the *ad hoc* laboratory, and they should, by means of periodical discussions, either over their meals or otherwise, keep absolutely in touch with all that was going on in the industry at large.

The duty of the great oil companies is twofold. They have, of course, the duty to their shareholders—*i.e.*, to pay their dividends—but they have also a duty, which he was not saying they do not realize or recognize—namely, a strong duty to posterity. They are trustees, for the time being, of the world's resources, and they have no right to waste those resources in any way whatever. They ought to put, to his mind, at least one-tenth of their income towards what is, to all intents and purposes, putting back in the form of knowledge what they took out of the earth in the form of oil. Ten per cent. of their income is a very large sum, he admitted; but still, it is not too large, and he would suggest that that is the sort of general propaganda which he would like to see carried out. He submitted that the youth of the present day is much too apt to jump to conclusions. Like an antelope, one could jump from point to point, and survey the country and so forth; seeing only what was visible from the particular point reached; but the intervening ground was passed over unexplored, and when one got sufficiently

far away from the base, it was often found that the pioneer had lost his way, and that the next distant point was too far away to reach. That led him up to the definite point that research, as research, is not the slightest good unless the ground between the base and the point one wishes to reach is thoroughly surveyed and made good. One could not make a discovery and then go on making others by what was really shooting in the dark; but one must make good every step one had passed; in order to progress further direction was essential. That is absolutely true of every kind of industrial research, and it is certainly true of petroleum research, which is, after all, a section of organic chemistry, dealing with the unsaturated hydrocarbons, substances about which very little indeed is known. It had been his privilege, in collaboration with Dr. E. H. Farmer, to write an article on the unsaturated hydrocarbons for that *magnum opus* which is shortly to appear in conjunction with themselves and their friends the Americans, and he had really been astonished at his lack of knowledge of those substances. Practically nothing is known about those compounds. The engineer is really the trouble: he invents an engine for which the chemist must find something in order to make it work, and he is apt to do that without a moment's notice. Just now he is changing over from the petrol engine to the Diesel engine, and before very long he will have an engine which will run on nitroglycerine, and then what would the chemist do?

Those were the points the speaker wanted to make in opening the discussion. The most important one he wished to emphasize was the necessity for doing all that could be done to foster fundamental research underlying the industry. If one did that, all the rest would follow. One might not get solutions of commercial value immediately, but no doubt they would come. Anyway, they would not come unless one made good every step of the way and progress by direction rather than by intuition. Newton has been dead more than 200 years, but his method is still the best.

There was an indication, he was sorry to say, of the prevalence of the thought that the buying of processes outside the country is adequate to the production of new processes in the petroleum industry. He did not think that was a subject upon which he need enlarge; it is so obviously wrong. Not only is it unfair to our own research men—because if the universities trained research men it is for the petroleum people and the other people in industry to employ them—but also in time of war we should look particularly silly if we found that we had to rely entirely upon some process which had originated in an enemy country. The country that can produce first-hand knowledge is the one that will survive in the terrible struggle with which the next generation will be faced, and although the method of buying new processes is of importance, yet if it becomes predominant the result will be fatal.

Professor Thorpe said that he had no intention by his remarks to indicate that no research work was being carried out in this country. That arose from the misreading of his Presidential Address to the Institute of Chemistry. There is, without question, good and admirable work being carried on, more particularly at Sunbury. What the speaker wished to emphasize, with all the force of which he was capable, was that there was not sufficient research of a fundamental kind being done, and that the amount of money allocated to this end was not enough.

COLONEL S. J. M. AULD said that as regards organized research work his view had always been in a direction exemplified by recollection of being in a tug-of-war team and testing out every man individually against a dynamometer. It was true that the whole team could not show anything like the additive individual efforts. But the fact remained that the eight men on the rope could do something that could not possibly be done by eight separate men. He thought that was the answer to nearly all of the research that was carried out at the present time for industrial purposes; it needed team-work, even at the expense of reduced individual efficiency. He was, he confessed, a little alarmed sometimes, even without having seen Mr. Vermeulen's chart, to think of research work of any kind, whether it was with a big R or whether it was with a little r, being mechanized; but that could not be helped: to get big results one must do things in a big way. Dr. Dunstan and he at one time used frequently to employ a catch-phrase that must still be in Dr. Dunstan's mind, which was a remark dropped by the celebrated Emil Fischer, who, in describing one of his researches, kept on saying, "Then we did another experiment." It has been in his mind that that was the answer to most things: it was the doing of the "other experiments," the carrying of them on and seeing exactly where one was, that was bound to supply the ultimate answer. How it should be done he was not clear—whether the right way was for the individual companies to have large experimental stations; whether it should be done by groups of industries; or whether the research centres should be the national research stations formed for various purposes here and there. These were questions on which he was not in a position to make up his mind. They all seemed to have points. It was perfectly true that in the industry in which most of those present earned their livings there were research organizations than which in their own line all the universities in the world could do no better. It was essential, however, that such organizations should, as the Chairman had pointed out, have their work centred around the day-to-day or year-to-year exigencies and difficulties of the industry, though it was from such things that the pointers towards basic work must and would arise. It was there that he parted company from Professor Thorpe. One must go back to the universities for the basic research, to fill in all the gaps, to get the actual principles on which one must work. It was perfectly true in chemical engineering practice that if one's principles were right, one could never be wrong; but if the principles were wrong one could have the most elaborate work carried out and it was bound ultimately to fail. In getting those fundamental principles one had to cater not necessarily for the exceptionally brilliant man, but almost certainly for the man with a temperament. The man with the temperament was not always safe in an industrial organization. It was, indeed, very difficult to cater for him anywhere. Dr. Dunstan wanted to shut him up and just make him lay an egg; but suppose he would not lay an egg under those conditions? In the university laboratories a man could always put his hat and coat on and say, "I am not going to work for two or three days; I am going for a walking tour." In the industrial laboratories he had not actually to punch the clock, but he was going to be cramped by the feeling that he was paid to produce something and that he had got to produce something.

Turning to a more individual aspect of the matter, he would like to hear

from Mr. Shepard what arrangements were made throughout a big organization like his own for keeping in touch with the actual requirements in the field. He had indicated all the relationships inside the organization, but how did he manage to keep in touch with the requirements of the industry outside? It was easy when one had refinery problems, because refineries were more or less on one's doorstep, and one could and did have an interchange of personnel. Even whilst saying it was "easy," he remembered that Dr. Dunstan, he was sure, had had a real difficulty to meet all his life, of changing men over so as to make sure that they really were in touch with the requirements (*a*) of the user, and (*b*) of the producing side, so as to ensure that the research had a practical aspect all the way through. He had noticed, at random, in Mr. Shepard's paper, however, a reference to launching grease. One obviously could not bring a ship into the research station and carry out experiments on it, and he would like to know, taking such a case as an example, what was done and how touch was kept with marine requirements. The same thing might happen in regard to the steel rolling mill business. He was interested to know what steps were taken to insure simulated tests being representative of practical needs.

Dr. E. R. Redgrove said that a great amount of research was, of necessity, wasted effort, and it was the elimination, as far as possible, of wasted effort which was the principal argument in favour of organized research, such as had been so admirably expounded by the authors of the two papers.

In most industries to-day research had been organized to a high degree either by firms operating independently or by means of Research Associations. From the point of view of public service the latter method was more desirable, because the cost could be borne proportionately by the whole industry, and the benefit to the concerns participating would be proportionate to their magnitude.

Although much had been done to co-ordinate research in industry, the effort was largely confined to industries amongst themselves, and it would seem that there was a real call for a system of liaison research, so that each industry could keep in touch with the progress being made in kindred industries. Such liaison would have to be carried out by what might be called "research Scouts," who would have to be very versatile and capable scientists. Adoption of this plan would be possible as between one research association and another, and would obviate the *impasse* which so frequently arose when one industry produced something which could not be put into service because it was ahead of its time and of the research of kindred industries, upon the products of which it must depend for its satisfactory and efficient operation.

Mr. E. H. Cunningham-Craig said he was beginning to wonder, when the President called upon him, whether the discussion on the organization of research in the petroleum industry had nothing to do with geology at all, whether it was confined only to chemistry; but he thought every geologist realized that there was a good deal of research in geology on petroleum that was very much needed. The next point he wanted to make was that research in petroleum—research that did include geology—should be made

in very close liaison with chemists. He had already, four times in his life, had the pleasure of doing certain specific researches in close liaison with a chemist, and each time the results had been fruitful; but he had never had enough of it, and he maintained that research—and though it might be called pure research, it always had a practical bearing upon the real, fundamental problems of petroleum—could not be conducted by the geologist solely, or solely by the chemist, but must be conducted by a combination of the two. For instance, to take the case of the famous German chemists who had produced those wonderful, and now more or less discredited, theories about the origin of petroleum, they had done wonderful work, but they had done it without any collaboration with geologists, and immediately a sort of definite split between geologists and chemists had been formed, to the detriment of both.

Another point was this: What was research in geology? It was rather difficult to say sometimes. Any mapping or development of a new country was to some extent research, but when one dealt with a well-known country, such as this country, which had been geologically mapped and studied, and had had memoirs of all kinds written about it, and when one came to study this country from a new point of view, the point of view of petroleum, which had hardly been known of in this country except in the last thirty or forty years, most of the work consisted of reading the memoirs and studying the maps that had been written or published many years ago. That, of course, was hardly research, but there were other points of research that could be taken up, and it was the lack of studying those other points that caused very costly experiments in drilling to be made, experiments which might have been avoided if enough geological research had been undertaken. But, as he had already said, geological research was not complete without co-operation with the chemists.

Mr. J. S. Jackson said that the organization of research presented an extremely complicated problem. Organized research called for human beings with all the virtues; but as these were seldom available, any such organization must of necessity be something of a compromise. Modern industry, of course, demanded organized research; but since modern industrial methods might not represent the best way of conducting human affairs, organization of research might not produce the best results. All the speakers had emphasized that the research worker was essentially an individual, and it was important that this individuality should be preserved. All efforts at organization tended to rob the research worker of that individuality. Normally one expected the individual research worker to be a man of ideas; but it was necessary to discriminate carefully between the processes of research and invention. He doubted very much whether the universities produced, or could produce, the inventive type of man. Research work was necessarily systematic, careful, patient, industrious, plodding work. The inventor, on the other hand, depended on inspiration or brain-waves. He might wake in the morning with an idea which resulted automatically in a brilliant invention. The inventor, in fact, was frequently not characterized by abnormal energy. The inventor usually did not come from the university. One of the most inventive men he had met was a man whose education stopped far short of the university, and it was just

because he had not been hampered by the views, experience and authority of others that he had been able to invent. He was inventive because he did not know of all the things that were said to be impossible. By the time a man had spent three or four years in a university he was hedged round with an immense number of things that were impossible, and he had been told that they were impossible by the superior people who had educated him. His mind was certainly trained, but it had also been disciplined. A man had to have a very remarkable mind and a very remarkable personality to leap such barriers and get out into the open country.

Strangely enough, nearly every chemist he had ever met regarded himself as a research chemist; therefore it seemed that a clear definition of research work was needed. Mr. Shepard's paper had given him the impression that the whole of his organization was peopled with research chemists. If research could begin in the refinery control laboratory, then of course every chemist might be a research chemist. Nevertheless, he would like to join with Mr. Shepard, and express the wish that every chemist could, and would, become a research chemist. Every chemist who had the necessary mentality, the necessary training and the necessary knowledge could become a research chemist. There was really no such thing as a routine job. Such a job might at any moment give rise to a most important research. The so-called routine job was probably dealing with some difficulty that had arisen in a manufacturing process, and if the chemist concerned did not regard such work from the research angle, then he was not doing his job. Unfortunately, great companies and great resources did not necessarily produce research. The real problem was to find the men with the right outlook, and the finding of men capable of doing research work properly and successfully was a very difficult matter. The research worker had to be not merely a brain, but a very complete human being with a multitude of other virtues, and it was just those virtues which were so hard to cultivate and to maintain under modern conditions. Once the research worker began to think of his salary, his efficiency was impaired. The true research worker had to be something of an artist. He had to be prepared to live for his work. In addition, he had to be honest and industrious, capable and modest, sincere and generous and, above all, prepared to co-operate freely with others. In fact, he had to be a very remarkable human being in this modern generation if he were to be a real, true research worker. He thought that the finding of these excellent but rare beings who could and would do such work for the benefit of humanity presented the real problem in connection with organized research work.

He was rather glad that the papers had been given, because they did something towards dispelling the entirely erroneous notion that there was little or no research work done in the petroleum industry.

A SPEAKER said that in connection with the Institution there was a Committee known as the Cancer Research Committee, and if it was not beside the point, he would like to be told something of the activities of that Committee. The Chairman's name, he believed, as well as other names, was associated with the Committee.

THE CHAIRMAN replied that the Institution did possess a Cancer Research

Committee, which in the past had been working in collaboration with the Manchester Committee on Cancer, and all he could say at the moment of the activities of the Committee was that it had discussed at various times and examined the evidence for and against the incidence of cancer in mule-spinners, and he could say that so far that Committee of the Institution had not been convinced by any means that that so-called incidence of cancer was in any shape or form connected with the use of spindle oils.

Ir. J. H. Vermeulen (in reply) thanked the speakers for their valuable contributions to the discussion. He had purposely not dealt with the philosophical side of the question of research, but had tried in his paper to give a concrete scheme of the organization of an existing central laboratory; and that was the difference between various speakers in the discussion and himself. The valuable papers of Dr. Dunstan and of Stine, and also the book by Boyd, were concerned principally with the theoretical side of the concept of research—*i.e.*, the division according to the types of research. He had tried to give a more concrete scheme, and when one had a laboratory of 300 or 400 laboratory workers it was impossible only to show the theoretical side.

Replying to the Chairman's remark, he would like to say that the separation into routine and research work offers the possibility of setting the research worker apart from routine and of allowing him to pursue his own mind. In this so-called " cell system " the desire to allow some workers who are worth it a large amount of freedom in their work, can be fully realized, notably by creating a " one-man cell " and leaving him—*i.e.* the cell--completely free in the choice of his subjects. In most cases such a " cell " will be a pure research cell.

In addition to Professor Thorpe's discussion, it can be said that the separation of research work *ad hoc* and long-distance research is about the same as that of Applied Research and Pure Research, and that the wishes as regards close contact between the industrial research laboratories and the Universities can be fully endorsed.

Mr. E. Cunningham Craig may be referred to page 2 of the paper, from which he will see that in the laboratory of the Royal Dutch Shell Group various chemical research problems are being dealt with that really belong to the domain of geology.

That close contact between the chemists working on these problems and the geologist is essential for the proper solution of such problems, may here be emphasized.

Mr. David A. Shepard (in reply) said he thought he would confine his comment to the question placed by Colonel Auld and the remarks of Mr. Jackson. Colonel Auld had asked why his Company had become interested in launching grease. It was one of the men accused by Mr. Jackson of being a research chemist—but actually, perhaps, not fulfilling Mr. Jackson's definition of a research chemist, because he probably thought of his salary from time to time—who had started the launching-grease problem which had been interesting them during recent months. It was largely because the problem was a recent one that the comment was included. As Colonel Auld had pointed out, it was a difficult matter to bring a ship into

the research laboratory. Just so was it difficult to carry out studies in a research laboratory on, for example, a 10,000-h.p. Diesel engine. The method, therefore, of making such studies offered a good example of the means by which a research organization could keep in touch with indications of future necessities and with present problems previously neglected. In the first place, there was an organization which he had mentioned very briefly in the paper, called the sales engineering department. The name had always been, in his opinion, rather misleading. It might, perhaps, be more accurately described as a research feeding organization. One of its very important jobs was, to speak in the vernacular, to keep an ear to the ground. It had very close contacts with the automotive industry and other industries important to petroleum marketers. It maintained those contacts by personal visits to a large number of units in those industries, and it served as a means to " feel the pulse " of the user of petroleum products. Many suggestions for studies of various problems flowed into the research organization from that body. So the launching grease problem was introduced. One of the large shipbuilders in America was not satisfied at the moment with the lubricant he was using under the hull of a ship about to be launched. From the suggestion given to the research organization by the contacting body an investigation of the launching grease problem was started with the shipbuilding organization. It appeared to him to be an interesting reference to the necessity of co-operation between a research organization and industry. Not only was there, as he saw it, a philosophical advantage in that co-operation, but there was also a very practical and concrete necessity. Not only must one fall back on specific organizations in other industries for assistance in guiding the research in the laboratory, or at least in making suggestions for that research, but one must also, of necessity, keep in close contact with such units for assistance in problems like that where one could not bring the ship into the laboratory.

On the motion of the Chairman, a vote of thanks was accorded to the authors by acclamation.

# REMARKS ON RESEARCH.

By Ir. G. D. Boerlage.

On the occasion of the Institution's visit to Holland in May, 1936, Mr. Boerlage, in his address of welcome to the visitors, contributed some views on research which, having more than a passing interest, are given a wider publicity in an abbreviated form hereunder :

Although these remarks are directed particularly to technical research at the Delft Laboratory of the Royal Dutch Shell Group, they may be applicable to other kinds of research work.

Technical research to-day goes beyond the confines of mechanical engineering. It requires a great deal of first-class physical and chemical assistance.

Nevertheless, it must be realized that there is a difference between these technical methods and physical and chemical methods. Technical research has a character of its own.

Engines are extremely complicated things, and there are occasions when an engineer will achieve more with his talent for psychology than with his mechanical knowledge. Engine behaviour is often most readily understood by a good physiognomist.

We are all, by nature, more or less capable physiognomists. The main value of this faculty lies not in its reliability, which is far from perfect, but in its swiftness of perception.

In one second a judgment is formed, and often it is a good one ! It might have taken hours, if not days, or longer, to determine exactly what features led to that judgment.

I am convinced that this wonderful faculty of reading character at first sight is of extreme importance in research work. It allows for quick orientation in the chaos of unknown possibilities.

The talent for physiognomy may take as its subject a man's face, an audience at a meeting, a landscape, a town or a home. It is the physiognomy of the chessboard that a great chess-player perceives at a glance; analysis may improve this judgment, but that process comes later.

Every problem has its physiognomy, differing according to the spectator and his personal reactions to the features it presents.

It is this faculty that is responsible for so many inventions by people in relatively poor circumstances. Why did human flight begin with men such as Lilienthal, Mouillard, Farman, or in the simple surroundings of a repair shop, and not in Universities ?

It is the artist in us that helps to solve difficult problems in a short time, and time is here the important factor. This holds true not only for inventors, explorers, business men, diplomats and generally for great historical characters, but also for the modest research men in our laboratories.

Many people who would say that " business is business," may assert that they are not artists, that they are realists, and that they possess no great

powers of imagination; but it is the opinion that is formed long before calm analysis which is attributable to the capacity for rapid reaction. Excessive confidence in that first conclusion has often resulted in the ruin of strong characters where the indispensable subsequent analysis was neglected.

This unusual faculty does not in any respect diminish the value of scientific research. On the contrary, such scientific research, together with observation, meditation and imagination, to say nothing of hereditary factors, brings material to the sub-conscious mind, and it is out of this material, stored in the sub-conscious mind, that suddenly arises the judgment by a process quicker than that of subsequent analysis.

A research organization may therefore as far as possible register systematically programmes and results, but there comes a great danger if it should interfere too much with the research man's work. A research worker should not feel his task a burden and a duty; he is at his best when he is fascinated by it. If, as far as is feasible, he is allowed to be free to make his mistakes, to lose time in vain efforts, to struggle without help—one day he may create a masterpiece of far greater value than what might have been produced under control.

When his task outgrows his activity, he should have friends—reliable friends, not such as will take the work out of his hands, but such as will supply what is beyond his reach. Friendship and confidence have often been more effective than knowledge in research; they are the bases for good team-work.

In short, research is to a large extent a subconscious investigation. Therefore a research organization, to be fruitful, should respect this characteristic.

That is what is felt about the organization of research in the Proefstation: the various departments in Delft have been made as far as possible autonomous; they are still so small that this can be tolerated.

Obviously, problems of the research organization will become more and more difficult as the size of laboratories increases.

A final word may be said about scientific contacts between workers inside and people outside the laboratory. Such encounters play a prominent part in all research undertakings. The Institution's visit is of the type that has proved to be extremely useful for the further development of research work. It brings new problems, opens up new horizons and makes new friends, and that is why you are so very welcome.

# THE DESULPHURIZATION OF OILS.

By C. M. Cawley, Ph.D., M.Sc.

The removal of sulphur frequently offers great difficulty in oil refining, and any proposed method of desulphurization is therefore worthy of attention. The work described in this paper was undertaken with a view to examining the value of carbon monoxide for the desulphurization of oils. In a recent paper, B. W. Malishev [1] showed, in a series of experiments, that carbon monoxide could be very effectively used for desulphurizing a solution of thiophene in toluene; in one experiment he found that a solution of heptyl sulphide in toluene could be similarly desulphurized, and, in two further experiments, that the sulphur content of a pressure distillate (which was stated to contain mainly "the most stable tetramethylthiophene") could be reduced by about 70 per cent.

Malishev studied the activity of a series of seven catalysts for desulphurization, and found that molybdenum trisulphide formed the most active agent. The apparatus he used was a rotating autoclave of 100 ml. capacity, and the experimental conditions were: a reaction temperature of 300° C., a pressure of carbon monoxide of 1000 lb. per square inch, and a period of heating, at 300° C., of 4 to 6 hours. For each experiment 50 ml. of oil were used. In the most successful experiment the treatment of a solution of thiophene in toluene containing 0·84 per cent. of sulphur yielded a liquid product containing only 0·06 per cent. of sulphur.

These results are in marked contrast with those obtained at the Fuel Research Station [2] in a brief investigation conducted to test the reported efficiency of carbon monoxide as compared with hydrogen for the desulphurization of oils. The experiments were conducted in a 2-litre rotating autoclave, and the amount of oil treated in each test was 150 ml. The reaction temperature was 365° C., the initial pressure 70 atmospheres, and the time of heating at 365° C. 4 hours. The catalyst consisted of molybdenum sulphide supported on alumina gel; it was prepared by impregnating alumina gel with ammonium molybdate, heating to 500° C. and finally sulphiding in a stream of hydrogen sulphide at atmospheric temperature and pressure. The oils treated for the removal of sulphur were a lubricating oil and a low-temperature tar oil boiling below 360° C. The gases employed

Table I.

*Sulphur Content of Raw Materials and Oil Products.*

| Material Treated. | Lubricating Oil. | Tar Oil. |
|---|---|---|
| *Sulphur content of oil, per cent.* | | |
| Original oil | 1·72 | 0·63 |
| Products from experiments with: | | |
| (*a*) Nitrogen | 1·54 | 0·44 |
| (*b*) Carbon monoxide | 1·39 | 0·36 |
| (*c*) Water-gas | 0·29 | 0·10 |
| (*d*) Hydrogen | 0·08 | 0·04 |

were : (1) nitrogen, (2) carbon monoxide, (3) water-gas and (4) hydrogen. The sulphur content of the raw materials and the products, given in Table I, showed that some sulphur was removed in all cases.

The results obtained from the experiments with nitrogen suggested that the greater part of the loss of sulphur in the experiments with pure carbon monoxide was probably due to the removal of sulphur by combination (*a*) with the iron of the walls of the converter to form ferrous sulphide, (*b*) with any remaining molybdic oxide in the supported catalyst and (*c*) with hydrogen in the oil or its decomposition products. Ferrous sulphide was found on the walls of the converter in small quantities in all experiments.

It was concluded that the reduction of sulphur content due to the action of carbon monoxide, although small, was perhaps not insignificant in view of the fact that optimum conditions were not determined.

Owing to the apparent disagreement between the two sets of results, it was decided to carry out, at the Fuel Research Station, a second series of experiments.

## Experimental Details.

Since the only apparatus available at the Fuel Research Station was a 2-litre rotating autoclave, it was obviously impossible to reproduce exactly the conditions employed by Malishev without using an excessively large quantity of the oil to be treated. It was therefore necessary to use either the high pressure of carbon monoxide employed by Malishev, and hence a large excess of carbon monoxide, or alternatively to use a pressure low enough to preserve Malishev's proportion of carbon monoxide to oil. The second alternative was decided upon, and the experimental conditions were then as follows :

| | |
|---|---|
| Solution of thiophene in toluene (0·90 per cent. sulphur) | 150 ml. |
| Initial pressure of carbon monoxide | 100 lb./sq. in. |
| Catalyst (molybdenum trisulphide) | 15 gm. |
| Reaction temperature | 300° C. |
| Time of heating at reaction temperature | 4 hours |

The catalyst was prepared by precipitation with sulphuric acid from an aqueous solution of ammonium thiomolybdate.

It was found that the sulphur content of the solution of thiophene in toluene was reduced from 0·90 to 0·07 per cent. It was evidently not necessary in this case to use the carbon monoxide at the high pressure employed by Malishev.

A series of experiments was accordingly carried out under the above conditions, but certain alterations were made in some experiments, as indicated in Table II. In order to test the efficiency of carbon monoxide and the precipitated catalyst, comparative experiments were conducted with (1) nitrogen, (2) a catalyst prepared by presulphiding the molybdenum catalyst supported on alumina gel and (3) various raw materials. The results of these experiments are recorded in Table II.

There was a small mechanical loss in most experiments, and the average yield of liquid product was therefore about 95 per cent. by weight. Analysis of the original and residual gases showed that cracking of the raw material occurred to only a negligible extent.

TABLE II.

*Sulphur Content of Oils Desulphurized with Carbon Monoxide.*

| Oil Treated. | Catalyst. | Gas Used. | Sulphur in Oil Treated, %. | Sulphur in Product, %. |
|---|---|---|---|---|
| Thiophene in toluene | $MoS_2$ pellets | CO | 0·90 | 0·07 |
| Thiophene in toluene | None | CO | 0·90 | 0·77 |
| Thiophene in toluene | Molybdenum sulphide supported on alumina gel | CO | 0·90 | 0·53 |
| Thiophene in toluene | $MoS_2$ pellets | $N_2$ | 0·90 | 0·76 |
| Once-run benzole | $MoS_2$ pellets | CO | 0·88 | 0·40 |
| Once-run benzole | $MoS_2$ pellets | $N_2$ | 0·88 | 0·46 |
| Tar oil | $MoS_2$ pellets | CO | 0·63 | 0·44 |
| Tar oil * | Molybdenum sulphide supported on alumina gel | $N_2$ | 0·63 | 0·44 |
| Lubricating oil | $MoS_2$ pellets | CO | 1·72 | 1·77 |

* Taken from the Report of the Fuel Research Board for the year ended 31st March, 1936, p. 108, Table 48.

## DISCUSSION OF RESULTS.

In a first experiment with the precipitated molybdenum trisulphide catalyst, as already recorded, the sulphur content of a solution of thiophene in toluene was reduced from 0·90 to 0·07 per cent. In a second experiment in which no catalyst was used, the sulphur content of the product was 0·77 per cent. The activity of the catalyst was thus demonstrated. Even when the supported molybdenum catalyst was employed, the sulphur content was only reduced to 0·53 per cent. There can therefore be no doubt that precipitated molybdenum trisulphide is an active catalyst for the process.

In order to test the efficiency of carbon monoxide as a desulphurizing agent, a " blank " experiment was conducted in which nitrogen was used in place of carbon monoxide. The sulphur content of the solution of thiophene in toluene was reduced from 0·90 to 0·76 per cent. It was therefore clear that carbon monoxide played an essential part in the reaction.

The efficacy of carbon monoxide for desulphurizing thiophene being established, it was necessary to extend the investigation to include some commercial products; those examined were a once-run benzole, and the tar oil and lubricating oil used in the previous Fuel Research experiments.[2] The first material to be tested was the once-run benzole. In the initial experiment with carbon monoxide it was found that the sulphur content of the oil was reduced from 0·88 to 0·40 per cent. The carbon monoxide thus appeared to be moderately effective, but an experiment with nitrogen in place of carbon monoxide gave an almost equal reduction : the sulphur content of the product was 0·46 per cent. The reduction was almost entirely due to the destructive decomposition of the sulphur compounds, or, alternatively, to the loss of sulphur by combination with the iron of the walls of the converter. In any case, the carbon monoxide played very little part in desulphurizing the benzole.

A similar result was obtained from the treatment of the low-temperature tar oil boiling up to 360° C. Some reduction in sulphur content was

effected, but this was no greater than had previously been obtained [2] in the experiment with nitrogen at 365° C.

Lastly, the lubricating oil was examined. Here the treatment with carbon monoxide under the standard conditions apparently brought about a small increase in sulphur content. This may have been due to contamination with sulphur from the catalyst, or to experimental error. Clearly carbon monoxide did not effect the desulphurization of this oil under the conditions employed.

In order to confirm that the small sulphur reduction obtained in these experiments was not due to the low pressure of carbon monoxide used, a further test was carried out with the lubricating oil which was treated under a pressure of carbon monoxide of 1000 lb. per sq. in.; the conditions were otherwise the same as those used in the previous experiments and given in the experimental section of this paper. It was found that the sulphur content of the lubricating oil was in this way reduced to 1·46 per cent. As might have been anticipated, therefore, the higher pressure of carbon monoxide did effect the removal of a greater amount of sulphur. The reduction, however, was still very small.

## Summary and Conclusions.

The results obtained by Malishev [1] in the desulphurization with carbon monoxide of a solution of thiophene in toluene were confirmed. At a temperature of 300° C., a pressure of carbon monoxide of 100 lb. per square inch, and in the presence of molybdenum trisulphide, which is an active catalyst for the reaction, the sulphur content of the solution was reduced from 0·90 to 0·07 per cent. Under similar conditions carbon monoxide was, however, not effective for the desulphurization of benzole, low-temperature tar oil or lubricating oil. Some reduction in sulphur could be effected at higher pressures of carbon monoxide, but the extent was still small; for example, at a pressure of carbon monoxide of 1000 lb. per sq. in. the sulphur content of a lubricating oil was reduced by only 15 per cent.

According to Malishev, the treatment of organic sulphur compounds with carbon monoxide causes the removal of sulphur as carbon oxysulphide. He found that thiophene, tetramethylthiophene and heptyl sulphide could be desulphurized in this way. From the results given in this paper, however, it would appear that in the present state of our knowledge the reaction is not generally applicable to organic sulphur compounds.

The work described above was carried out as part of the programme of the Fuel Research Board, and is published by permission of the Department of Scientific and Industrial Research.

*References.*

[1] *J. Inst. Pet. Tech.*, 1936, **22**, 341.
[2] Report of the Fuel Research Board for the Year ended 31st March, 1936, p. 107.

# A TABLE OF SPECIFIC GRAVITY CORRECTION FACTORS FOR PETROLEUM OILS.

By E. S. L. Beale, M.A., F.Inst.P. (Member).

Synopsis.

The well-known Bureau of Standards Circular No. 154 has been taken as the basis for the calculation of a standard table of specific gravity correction factors, which are shown to give the same results when used in the ordinary way as the elaborate tables in the Circular.

The method adopted has been to calculate the mean correction over the temperature range 60° to 120° F. from the tables for oils of S.G. 0·726 and heavier, and over the range 60° to 90° F. for oils lighter than 0·726. These values were plotted on a large-scale graph, and this was then divided into steps of 0·00001 per ° F, and the range of S.G. over which each of these is applicable was read from the curve.

Attention is directed to the additional errors introduced by the use of the Abridged Volume Correction Table issued by the A.S.T.M., which is based on the same data as Circular No. 154, and also the errors which may be caused by a considerable change in the apparent value of the correction factors of waxy oils at low temperatures.

A fairly extensive investigation into the thermal expansion of American Petroleum Oils was made by the U.S. Bureau of Standards from 1912 to 1915, and the results were published in their Technologic Paper No. 77 in August, 1916. From these experimental results, which cover the range 0° to 50° C., extensive tables were calculated for the reduction of volumes and specific gravity to 60° F. These tables are contained in the well-known Circular No. 154 entitled the "National Standard Petroleum Oil Tables."

These tables have been in general use in the United States for many years, and therefore have a strong claim to be the basis for general use, in spite of the fact that the average properties of petroleum oils as marketed to-day would be appreciably different from those of 1916, owing to the advent of cracking.

Table 3, in the Circular, is designed for reducing the specific gravity at any temperature observed with a glass hydrometer to 60° F., and occupies more than 100 pages of print. With this table the observed specific gravity can be reduced to 60° F. without calculation, but it has been the established practice in many oil companies to make this reduction by means of a simple, specific gravity correction factor which involves only a small amount of arithmetic, and thereby enables one to dispense with elaborate tables, and to use instead a short list of these correction factors. The formula is of course :—

$$S_{60} = G_t + a(t^\circ - 60^\circ \text{ F.}) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Where $G_t$ = the specific gravity at $t^\circ$ F.
and $a$ = the specific gravity correction factor per ° F.

Now, it should be noted that Circular 154 is not based on a set of correc-

tion factors which remain constant for each oil over the normal temperature range, but on a formula of the type :—

$$S_{60} = G_t + a(t - 60) + b(t - 60)^2 \quad . \quad . \quad . \quad . \quad (2)$$

Clearly therefore the average correction factor over the temperature range 60° F. to $t$° F. will vary somewhat with the value of $t$ chosen in cases where $b$ is not zero. In other words, the temperature–specific gravity plot will be somewhat curved.

## Effect of Curvature.

Before it is possible to prepare a standard table of correction factors which will adequately represent these tables, we must examine the practical effect of this curvature over the normal working temperature range and decide on the most satisfactory temperature range over which the factor chosen shall agree exactly with the table.

These two things are, of course, bound up with each other, and are best dealt with together by means of an example.

Examination of Table 10 on page 18 of Technologic Paper No. 77 shows that the oils with the greatest value of $b$ in equation (2) above occur at each end of the scale of specific gravities; oils the gravity of which lies between 0·780 and 0·840 having a value of $b$ equal to zero. Our examples should therefore be chosen from oils of high and low gravities so as to include the worst cases of curvature.

## High Gravity Oils.

For reasons which will appear later, we will choose the temperature range 60° to 120° F. as that over which the correction factor will agree exactly with the figures in Table 3 in Circular 154.

Choosing for this example an oil of specific gravity 0·956 at 60° F.[1]

From Table 3 (Circular) this would have a specific gravity of 0·9353 at 120° F.

The difference is 0·0207 in specific gravity and 60° F. in temperature.

Therefore the average specific gravity correction factor over this range is 0·000345 per ° F.

Now, taking this value for the correction factor and using it to calculate the specific gravity at 90° F., at which the effect of curvature would be most pronounced in this temperature range, we obtain :—

$$G_{90} = 0{\cdot}956 - (0{\cdot}000345 \times 30° \text{ F.}) = 0{\cdot}94565.$$

Whereas from the table we obtain 0·9455.

The difference between the tabular value and the value calculated with this constant correction factor is only 0·00015 in specific gravity, which is quite negligible.

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[1] This corresponds to an oil of density 0·950 at 25° C., which is the heaviest oil given in Table 10 in Technologic Paper No. 77, the results for which have been checked by independent calculation.

Similarly at 30° F. we obtain :—

| | |
|---|---|
| Calculated value . . . . | 0·96635 |
| Tabular value . . . . | 0·9667 |
| Difference . . . . | 0·00035 |

This difference is again negligible, particularly when the errors which would be introduced from other sources at a low temperature with such a heavy oil are considered.

Continuing this process to high temperatures and tabulating the differences we get :—

| Temperature. | Error in Calculated Value. |
|---|---|
| 30° F. | −0·00035 |
| 60 | 0 |
| 90 | +0·00015 |
| 120 | 0 |
| 150 | −0·00005 |
| 180 | −0·00004 |
| 195 | −0·0006 |

This table shows that all errors are negligible, and also, incidentally, that the errors are within the limits of accuracy with which the Table 3 (Circular) is calculated, as it is easily shown that with a constant value of $b$ in equation (2), the error should increase more at the higher temperatures than is given in the above table of errors. By choosing a temperature as high as 120° F. for zero error in calculating the average correction factor we get negligible error both at high temperatures and at low.

This procedure has therefore been adopted for all oils for which the values are given at 120° F. in Table 3. Below 0·726, however, the highest temperature given in the table is 90° F., and the temperature range 60° to 90° F. has therefore been chosen for oils below this gravity, as that over which the mean value of the specific gravity correction factor is calculated.

### Light Oils.

Choosing for this example practically the lightest oil given in Table 3—namely, one with a specific gravity at 60° F. of 0·620 from the table, the specific gravity at 90° F. is 0·6035, which gives an average correction factor of 0·00055 per ° F.

Calculating the specific gravity at various temperatures with this factor and comparing the values with those from Table 3, we get the following differences :—

| Temperature. | Error in Calculated Value. |
|---|---|
| 30° F. | +0·00010 |
| 60 | 0 |
| 75 | +0·00005 |
| 90 | 0 |

Here again the errors are negligible.

## Construction of Standard Table.

Having established that it is possible to use a fixed value for the specific gravity correction factor for each oil which will represent Table 3 of Circular

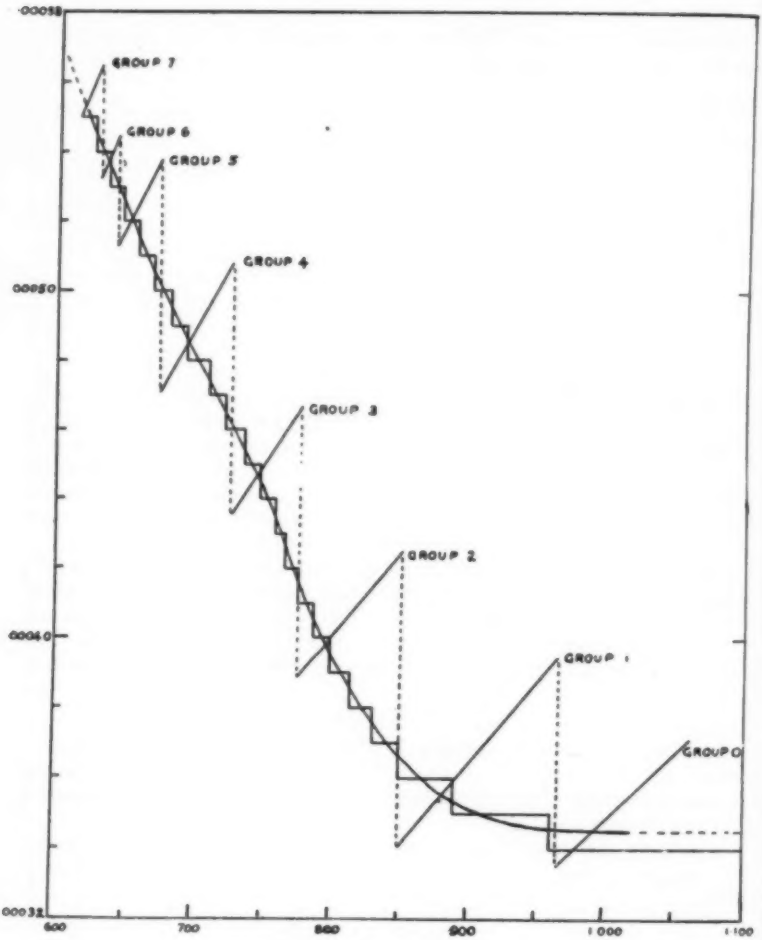


Fig. 1.

154 with the required accuracy, the next step is to settle on the representative range of temperature for each oil and calculate the average correction factor over this range for each oil.

For the reasons given and, it is hoped, justified above, the temperature ranges chosen are :—

60° to 120° F. for oils of S.G. 0·726 and heavier.
60° to 90° F. for oils lighter than 0·726.

The correction factors calculated in this way have been plotted on a large-scale graph against the specific gravity at 60° F. and are shown in Fig. 1.

For general use it is undesirable to have more than two significant figures in the correction factor for simplicity in calculation, and furthermore a higher degree of accuracy than this is not justified by the data on which these figures are based.

This does not imply that the experimental work is inaccurate, but that the variation between oils of different types is greater than the error of approximating in this way.

The correction factors in the following table have therefore been given to two significant figures only, and the range of specific gravity over which each factor is applicable is given to three figures. The specific gravity range for each step in the correction factor has been taken from a large-scale graph similar to Fig. 1, so as to give the minimum deviation on each side of the smooth curve. In this way the departure from the smooth curve is never more than 0·000005, whereas if the specific gravity range were also approximated to two figures the departure would be two or three times this amount in places.

The curve representing the Bureau of Standards figures is for use with a glass hydrometer. When calculating tonnages, the Bureau of Standards figures should really be corrected for use in steel tanks, by the difference between the correction factor in glass and in steel, but this difference is not large (0·000003 to 0·000005), and it has been thought best to leave them unaltered.

The only influence this consideration has had in the preparation of the following table of correction factors is in deciding to approximate the value of 0·000345 for high gravity oils to 0·00034 instead of 0·00035.

A Standard Table of Specific Gravity Correction Factors for Petroleum Products.

| Specific Gravity at 60° F. | Correction Factor per ° F. | Specific Gravity at 60° F. | Correction Factor per ° F. |
|---|---|---|---|
| Over 615 to 625 | 0·00055 | Over 746 to 756 | 0·00044 |
| „ 625 „ 635 | 0·00054 | „ 756 „ 765 | 0·00043 |
| „ 635 „ 645 | 0·00053 | „ 765 „ 775 | 0·00042 |
| „ 645 „ 656 | 0·00052 | „ 775 „ 786 | 0·00041 |
| „ 656 „ 667 | 0·00051 | „ 786 „ 798 | 0·00040 |
| „ 667 „ 680 | 0·00050 | „ 798 „ 814 | 0·00039 |
| „ 680 „ 692 | 0·00049 | „ 814 „ 830 | 0·00038 |
| „ 692 „ 707 | 0·00048 | „ 830 „ 850 | 0·00037 |
| „ 707 „ 720 | 0·00047 | „ 850 „ 890 | 0·00036 |
| „ 720 „ 734 | 0·00046 | „ 890 „ 960 | 0·00035 |
| „ 734 „ 746 | 0·00045 | 960 and over | 0·00034 |

## The A.S.T.M. Abridged Volume Correction Table.[1]

There is another method by which the necessary temperature correction can be applied without the use of the elaborate tables in Circular 154—namely, by using the Abridged Volume Correction Table issued by the A.S.T.M. This table is based on exactly the same data as Circular 154, but in the process of abridgment very substantial errors are introduced, and it is desirable that these inaccuracies should be clearly realized.

In order to reduce the size of the tables in Circular 154, oils have been divided into eight groups, according to specific gravity, and a given coefficient of expansion is used for each group. By limiting the number of groups to eight, a considerable error is introduced, due to attributing the same characteristics to the oils at the two ends of a relatively large group as to those at the middle.

This much is clear from general considerations, but unfortunately the fact that the coefficient of expansion is the basis for such a table, and not the specific gravity correction, makes this effect very much more serious. This can best be seen by converting the coefficients of expansion used in this abridged table to specific gravity correction factors and plotting the result against the true figures from Circular 154, which is based on the same data.

This has been done in Fig. 1. It will be seen that, whereas the true correction factor *decreases* with rising specific gravity, the assumed correction factors within each group *increases* with rising specific gravity. This results in a very substantial error in the assumed correction factor at the ends of the groups.

As an example, if the volume of an oil at the junction of Groups 1 and 2 is read from the table for 149° F. which is the maximum temperature range given, we get :—

| | |
|---|---|
| For Group 1 . . . . . | 0·9651 |
| For Group 2 . . . . . | 0·9558 |

which differ by nearly 0·010 or 1%.

## Advantages of Specific Gravity Correction Factors.

It will readily be seen that, apart from the relatively large steps adopted for the table, the main cause of error is the discrepancy in slope between the true and assumed correction factors. It naturally follows, therefore, that if a constant value of the specific gravity correction factor is used for each group giving horizontal steps on the diagram, this discrepancy is very greatly reduced, particularly for the higher gravity oils, where the true curve is itself horizontal.

Unfortunately, unless the coefficient of expansion is taken to be constant for each group, a short table of volume corrections cannot be compiled, so that we can say that a short and accurate table of this type is impossible.

It appears therefore that the use of a standard table of specific gravity correction factors such as the one given above is to be recommended in preference to any abridged volume correction table.

[1] Revised A.S.T.M. Standard Abridged Volume Correction Table for Petroleum Oils. A.S.T.M. Designation : D206 (1934).

## Waxy Oils.

There is one important fact in connection with the use of specific gravity correction factors or conversion tables of any kind which should be more generally appreciated—namely, that the correction factor of most waxy oils is far from being constant over the normal temperature range at which this is applied. This is due to the change in volume of the wax which crystallizes from solution as the oil is cooled, resulting in a very considerable increase in the apparent specific gravity correction factor at low temperatures.

The values given in Circular 154, on which the above table of correction factors is based, refer to the change in specific gravity of the oil itself, and

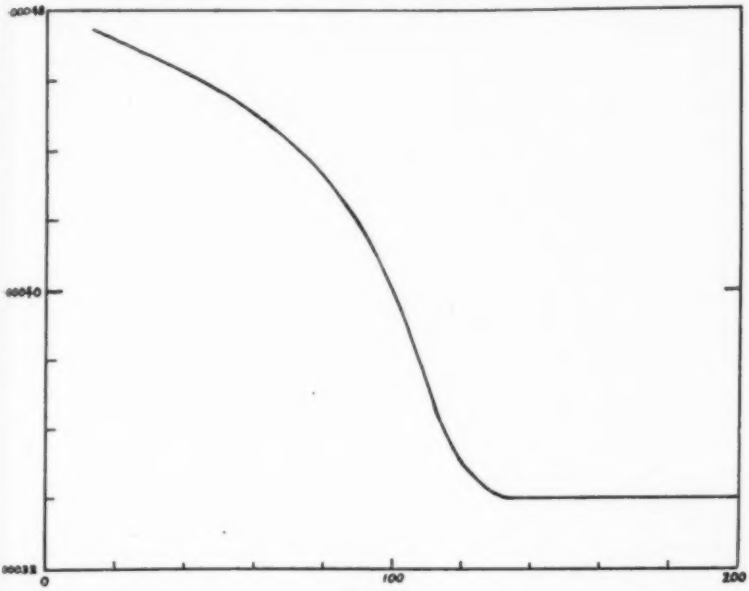


Fig. 2.

agree well with the behaviour of waxy oils at the higher temperatures where all the wax is in solution.

Moderately waxy fuel-oil of S.G. 0·925 may have a correction factor of 0·00034 per ° F. at temperatures above 130° F., whereas at 60° F. the correction factor for the same oil may be over 0·00045 per ° F., as shown in Fig. 2. If the specific gravity of an oil of this type is corrected from 130° to 60° F. by means of the normal factors suitable for non-waxy oils, the error will be in the region of 0·003 in specific gravity.

It is clear, therefore, that for tonnage calculations the specific gravity of waxy oils should be measured close to the temperature at which it is required, so as to avoid the very substantial error involved in correcting over a wide temperature range.

# THE ANILINE POINTS OF HYDROCARBONS.

By E. B. Evans, Ph.D., M.Sc., A.I.C. (Member).

The solution temperatures of hydrocarbons in various solvents have for some years been recognized as affording valuable aid in the characterization of pure substances and in the analysis of hydrocarbon mixtures. Of the several solvents which have from time to time been suggested for this purpose, benzyl alcohol and nitrobenzene are useful in certain cases, but the most generally convenient liquid which has been proposed is undoubtedly aniline.

Chavanne and Simon [1] suggested this method of analysis and determined the critical solution temperatures of a number of hydrocarbons in aniline, and suggested the estimation of aromatics by multiplying the difference in C.S.T. before and after the removal of the aromatics, by a suitable factor. An advance was made by Tizard and Marshall,[2] who proposed to use, instead of the cumbrous and time-consuming critical solution temperature, the far more conveniently determined aniline point, *i.e.*, the temperature of miscibility of equal volumes of aniline and the hydrocarbon. It is very surprising that this eminently practical suggestion has not been universally adopted, since the advantages are obvious, and there is no particular theoretical consideration attaching to the C.S.T. in this connection. The reason has been, perhaps, that at the time their suggestion was made a fair amount of data had been accumulated in terms of the older value.

Much of the earlier data recorded for the C.S.T.'s of hydrocarbons is, however, now of little value, as it is for various reasons inaccurate, and it is unfortunate that carefully determined figures on pure compounds still continue to be given in this form.

The solution temperature method is very widely used in the analysis of gasolines and kerosenes. Considerable confusion exists, however, between critical solution temperatures and aniline points, and the terms and data are used indiscriminately in many cases in the literature, although the results may in some instances differ very considerably.

The main sources of error which may arise in the determination of aniline point data may be divided into two classes. In many cases insufficient care has been taken to obtain pure compounds on which to carry out the measurements, and the resulting figure can easily be several degrees out on this account, since the solution temperature is a very sensitive property. The other main source of error is the use of impure aniline. The effect of water content in raising the aniline point has been emphasized by Ormandy and Craven,[3] but the importance of other impurities, such as nitrobenzene, which act in the opposite direction, does not seem to have been adequately recognized. (Erskine [4] gives — 11·5° C. as the C.S.T. of *n*-heptane in nitrobenzene, whereas the C.S.T. in aniline is 69·9° C., and the aniline point is 69·4° C.) In consequence of these misapprehensions, we find figures of from 68·8° C. to 71·0° C. recorded in the literature for the

aniline point of such an important hydrocarbon as *n*-heptane. There is, however, no difficulty at all in obtaining a pure aniline for this purpose if a good (A.R.) quality material be dried for 24 hours over stick potash or quicklime, separated and distilled, rejecting a generous proportion of forerunnings and tails, suitable precautions being taken to prevent the absorption of moisture during the distillation. The aniline thus obtained is quite stable in storage, and should give an aniline point of 69·4° C. with *n*-heptane prepared by sulphonating and fractionating the material supplied as a knock-rating standard.

In the course of work on the knock-rating and other properties of hydrocarbons, a number of determinations of aniline points has been made, using compounds of a high degree of purity. These results, together with other reliable data from the literature, are included in Table IV. Shepard, Henne and Midgley [5] record the C.S.T.'s of a number of pure normal paraffin hydrocarbons, their results being in very good agreement with data by Bruun and Hicks-Bruun,[6] and by Edgar and Calingaert.[7]

In addition to C.S.T.'s, Shepard, Henne and Midgley also give curves showing solution temperatures in aniline with varying amount of aniline, and from these curves the aniline points of the hydrocarbons may be obtained. Table I shows a comparison between the C.S.T.'s and aniline points from their results; it will be noted that the differences decrease progressively from 0·7° C. for *n*-pentane to 0·0° C. for *n*-nonane and the higher members.

TABLE I.

*Results from Shepard, Henne and Midgley.*

| Hydrocarbon. | C.S.T. | Aniline Point. | Difference. |
|---|---|---|---|
| *n*-Pentane | 71·4 | 70·7 | +0·7 |
| *n*-Hexane | 69·0 | 68·6 | +0·4 |
| *n*-Heptane | 69·9 | 69·4 | +0·5 |
| *n*-Octane | 71·8 | 71·7 | +0·1 |
| *n*-Nonane | 74·4 | 74·4 | +0·0 |
| *n*-Decane | 77·5 | 77·5 | +0·0 |
| *n*-Undecane | 80·6 | 80·6 | +0·0 |
| *n*-Dodecane | 83·7 | 83·7 | +0·0 |

TABLE II.

| Hydrocarbon. | Chavanne and Becker. C.S.T. | Garner and Evans. Aniline Point. | Difference. |
|---|---|---|---|
| *cyclo*Pentane | 18·0 | 16·8 | +1·2 |
| Methyl*cyclo*pentane | 34·7 | 33·0 | +1·7 |
| Ethyl*cyclo*pentane | 38·7 | 36·7 | +2·0 |
| 1 : 3-Dimethyl*cyclo*pentane | 45·0 | 44·5 | +0·5 |
| *n*-Propyl*cyclo*pentane | 50·5 | 48·7 | +1·8 |
| *n*-Butyl*cyclo*pentane | 48·8 | 46·4 | +2·4 |
| *cyclo*Hexane | 31·0 | 30·2 | +0·8 |
| Methyl*cyclo*hexane | 41·0 | 39·5 | +1·5 |
| *o*-Dimethyl*cyclo*hexane | 42·1 | 43·3 | −1·2 |
| *m*-Dimethyl*cyclo*hexane | 49·7 | 47·8 | +1·9 |
| *p*-Dimethyl*cyclo*hexane | 48·0 | 47·8 | +0·2 |

TABLE III.

| Hydrocarbon. | C.S.T. | Aniline Point. | Difference. |
|---|---|---|---|
| Pentene-1 | 19·3 | 19·0 | +0·3 |
| Hexene-1 | 22·9 | 22·8 | +0·1 |
| Heptene-1 | 26·6 | 27·2 | −0·6 |
| Octene-1 | 32·8 | — | — |
| Nonene-1 | 38·6 | 38·0 | +0·6 |

TABLE IV.

*The Aniline Points of Pure Hydrocarbons.*

| Hydrocarbon. | Aniline Point in ° C. | Hydrocarbon. | Aniline Point in ° C. |
|---|---|---|---|
| *Paraffins.* | | cyclo*Pentanes.* | |
| *n*-Pentane | 70·7 | *cyclo*Pentane | 16·8 |
| *iso*Pentane | 75·7 | Methyl*cyclo*pentane | 33·0 |
| *n*-Hexane | 68·6 [8] | Ethyl*cyclo*pentane | 36·7 |
| *n*-Heptane | 69·4 | 1 : 3-Dimethyl*cyclo*pentane | 46·4 |
| 2-Methylhexane | 74·0 [7] | *n*-Propyl*cyclo*pentane | 44·5 |
| 3-Methylhexane | 70·0 [7] | *n*-Butyl*cyclo*pentane | 48·7 |
| 3-Ethylpentane | 65·7 [7] | | |
| 2 : 2-Dimethylpentane | 77·6 [7] | cyclo*Hexanes.* | |
| 2 : 3-Dimethylpentane | 67·7 [7] | *cyclo*Hexane | 29·9 |
| 2 : 4-Dimethylpentane | 78·8 [7] | Methyl*cyclo*hexane | 39·5 |
| 3 : 3-Dimethylpentane | 70·5 [7] | Ethyl*cyclo*hexane | 43·8 |
| 2 : 2 : 3-Trimethylbutane | 72·2 [7] | *o*-Dimethyl*cyclo*hexane | 43·3 |
| *n*-Octane | 71·7 [8] | *m*-Dimethyl*cyclo*hexane | 47·8 |
| 2 : 2 : 4-Trimethylpentane | 79·5 | *p*-Dimethyl*cyclo*hexane | 47·8 |
| *n*-Nonane | 74·4 [8] | *n*-Propyl*cyclo*hexane | 49·8 |
| *n*-Decane | 77·5 [8] | *n*-Butyl*cyclo*hexane | 54·4 |
| *n*-Undecane | 80·6 [8] | 1 : 3 : 5-Trimethyl*cyclo*hexane | 55·5 [11] |
| *n*-Dodecane | 83·5 | Hexamethyl*cyclo*hexane | 65·5 [11] |
| *n*-Hexadecane | 95·1 | | |
| | | *Cyclic Olefines.* | |
| *Olefines.* | | *cyclo*Pentene | Below −10·0 |
| Pentene-1 | 19·0 | Methyl*cyclo*pentene | − 7·0 |
| Pentene-2 | 18·3 | Ethyl*cyclo*pentene | 1·2 |
| Trimethylethylene | 12·8 | *n*-Propyl*cyclo*pentene | 14·2 |
| Hexene-1 | 22·8 | *n*-Butyl*cyclo*pentene | 25·0 |
| Hexene-2 | 26·0 | *cyclo*Hexene | Below −20·0 |
| Heptene-1 | 27·2 | | |
| Octene-1 | 32·5 | *Bicyclic Naphthenes.* | |
| Di*iso*butylene | 42·8 | Decahydronaphthalene | 35·3 |
| Nonene-1 | 38·0 | Dicyclopentyl | 35·8 |
| Hexadecene-1 | 72·4 | *cyclo*Hexyl*cyclo*pentane | 42·5 |
| | | Dicyclohexyl | 42·5 |
| | | Dicyclohexylethane | 61·0 |

[8] Results converted from Shepard, Henne and Midgley.
[7] Results converted from Edgar and Calingaert.
[11] Results from Waterman, Dros and Tulleners.

A similar comparison may be obtained by tabulating the C.S.T.'s for a number of naphthene hydrocarbons, determined by Chavanne and Becker,[8] and aniline points for the same compounds recorded by Garner and Evans.[9]

The differences in this case vary from 0·5° C. to 2·4° C.—leaving out of account the dimethyl*cyclo*hexanes, which are mixtures of *cis*- and *trans*-

isomers. In the case of the α-olefines, the C.S.T.'s are only from 0·1° C. to 0·6° C. above the aniline points—as is shown by a comparison of the C.S.T.'s recorded by Wilkinson,[10] and aniline points determined on the same samples.

It may be remarked that no compound containing an aromatic nucleus has been examined the aniline point of which is not well below 0·0° C., and, in consequence, no data are given for this class of compound.

The analysis of gasolines by the aniline point method has been placed on a satisfactory basis by Garner.[12] The factors given there for the aniline

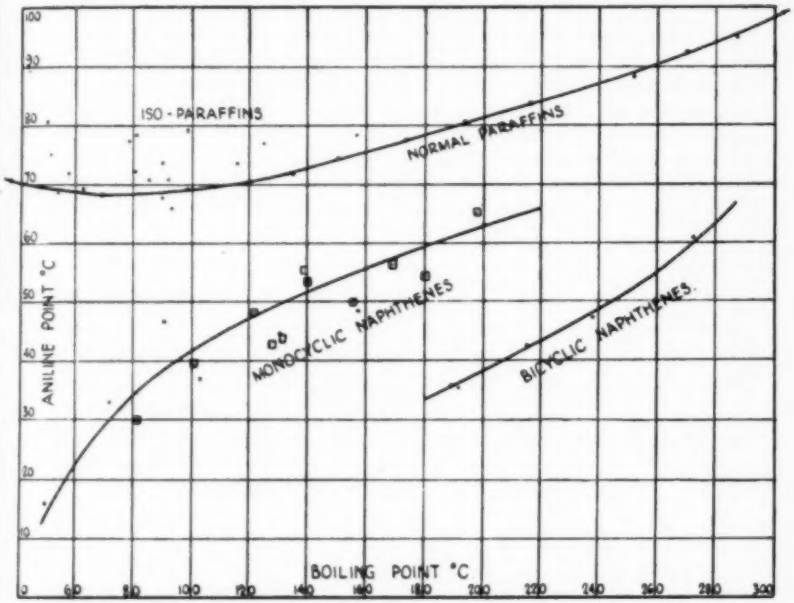


FIG. 1.

ANILINE-POINTS OF PURE HYDROCARBONS.

point depressions due to naphthenes and olefines are in good agreement with the results given here (see Figs. 1 and 2).

As regards the depressing effect of aromatic hydrocarbons on aniline point when mixed with paraffin or naphthene hydrocarbons, the available data are not very consistent. Tizard and Marshall [2] state that the depression caused by 20 per cent. weight of aromatics is 18·1° C., or 0·905° C. for each 1 per cent. weight aromatics, and that this effect is roughly the same for benzene, toluene or xylene, whether they be dissolved in gasoline, heptane or *cyclo*hexane. Carpenter [13] gives different figures. Using a toluene–xylene mixture (1 : 3 by volume), he found a depression of 0·856° C. in Burmah aromatic-free kerosene (Aniline Point 69·6° C.) and 0·864° C. in American aromatic-free kerosene for each 1 per cent. weight of the

aromatic mixture. Average results for addition of 20 per cent. weight aromatics derived from kerosene to aromatic-free kerosenes showed a depression of 0·81° C. for each 1 per cent. weight.

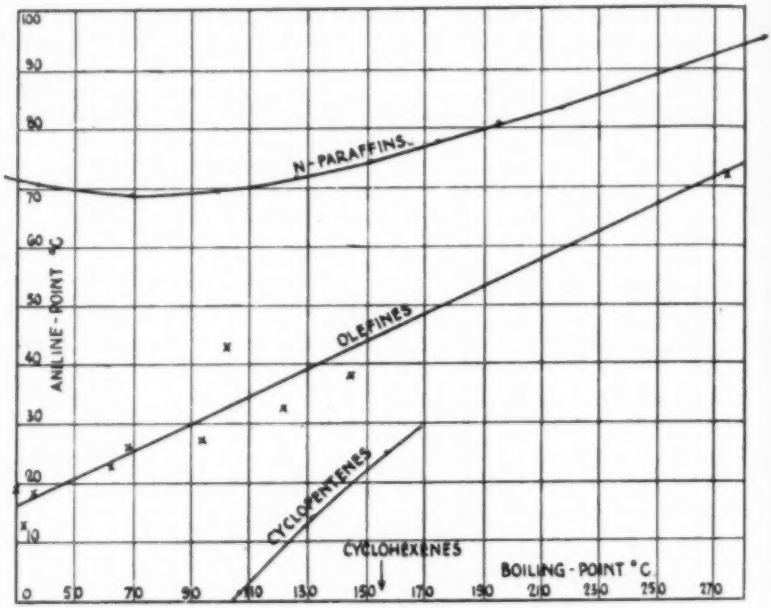


FIG. 2.

ANILINE-POINT DEPRESSION BY OLEFINES.

TABLE V.

| Hydrocarbon. | Boiling Point in ° C. | Depression for 1%. |
|---|---|---|
| Benzene | 80·4 | 0·85 |
| Toluene | 110·4 | 0·87 |
| *o*-Xylene | 141·5 | 0·875 |
| *p*-Xylene | 135·7 | 0·845 |
| Ethylbenzene | 136·1 | 0·86 |
| *n*-Propylbenzene | 158·6 | 0·825 |
| *iso*Propylbenzene | 153·2 | 0·79 |
| Mesitylene | 164·4 | 0·79 |
| *n*-Butylbenzene | 182·6 | 0·80 |
| *sec.*-Butylbenzene | 173·5 | 0·755 |
| *tert.*-Butylbenzene | 166·5 | 0·765 |
| *p*-Cymene | 176·5 | 0·745 |
| *tert.*-Amylbenzene | 190 | 0·725 |
| Tetrahydronaphthalene | 207 | 0·795 |

In Table V are given the results of determinations of depression of aniline point for 1 per cent. weight of a number of hydrocarbons in 20 per cent.

weight solution in *n*-heptane. It will be seen that these values are all considerably smaller than those given by Tizard and Marshall, but are in excellent agreement with the results of Carpenter.

Similar discrepancies occur in the values given in the literature for the depressions due to naphthenes, particularly in the gas oil range. Thus, Carpenter [13] proposed a factor of 0·2° C. depression for each 1 per cent. of naphthenes in the kerosene range, while Griffith [14] uses a factor of 0·4° C. in the analysis of gas oils. There has been considerable discussion on this point by Griffith and Hollings,[15] and Waterman, Vlugter and van Westen,[16] who have also worked on the composition of hydrocarbon oils, but who rely chiefly on refractivity data for this purpose.

Fig. 1 shows the variation of aniline point with boiling point for the few fairly high-boiling naphthenes for which data are available. The figure of 0·2° C. would be approximately correct for the higher-boiling monocyclic naphthenes, whilst 0·3–0·4° C. appears nearer for the dicyclic compounds. The naphthenes in kerosene and gas oil are without doubt mixtures of compounds with varying numbers of rings, and the available data, either as regards pure compounds or the occurrence of naphthenes in these petroleum fractions, are too meagre to permit a solution of the problem for the present.

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# THE PRINCIPLES OF SOLVENT DEWAXING.

## 1. Equilibria and Computations for Single Solvent Systems.

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During the last five years the principles of solvent extraction have been investigated extensively by the two senior authors.[1, 2, 3, 4] These investigations have led, among other things, to a graphical method of representing equilibrium data for complex oil–solvent systems.[4, 5] Computation methods based on such equilibrium diagrams have also been presented, and are now in use by many workers.[6] These principles and methods are, however, by no means confined to solvent extraction problems and processes and may be applied with success to other physical refining processes.

Although the process of dewaxing lubricating-oil stocks by means of the addition of a diluent or solvent has been in use for some years, no attempt has so far been made to examine the fundamental principles of such processes or to place them on a quantitative basis. This paper is an attempt to investigate the dewaxing process on a basis of graphical equilibrium representation and computation.

The equilibria involved in dewaxing operations are equilibria between a solid phase or solid phases, paraffin wax, and a complex liquid mixture of hydrocarbons, oil, together with a second liquid, solvent or diluent. Before considering equilibria in such a system, the simplest system involving a single solid component and two liquid components will be described.

### Equilibrium in a Simple Three-Component Solid–Liquid System.

A system consisting of three components $A$, $B$ and $C$ may be regarded as a combination of the three binary systems $AB$, $BC$ and $CA$. Fig. 1 represents the equilibrium data for the separation of solid from the binary system $AB$, where temperature is plotted as ordinate against composition. $T_A$ and $T_B$ are the melting points of the two pure components $A$ and $B$. It will be seen from this diagram that the addition of a small amount of one component to the pure melt of the other component lowers the temperature of equilibrium between solid and liquid. Curve $T_AE$ represents liquid mixtures of $A$ and $B$, of steadily increasing concentration in $B$, which are in equilibrium with solid $A$. Similarly curve $T_BE$ represents liquid mixtures of steadily increasing concentration in $A$ which are in equilibrium with solid $B$. Any mixture of components corresponding to a point such as $P$ will resolve itself into pure solid $B$ (point $R$) and a liquid mixture of $A$ and $B$ represented by point $Q$ on $T_BE$. The horizontal straight line $QPR$ is a tie-line indicating equilibrium between pure solid $B$ and the liquid mixture of $A$ and $B$ of composition $Q$.

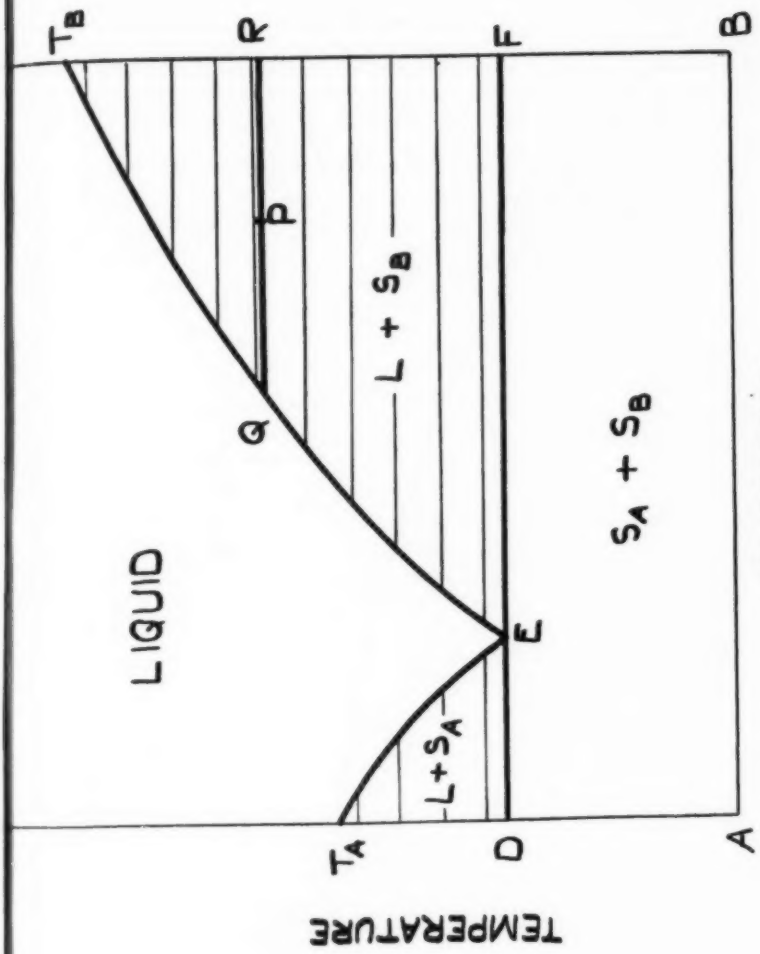
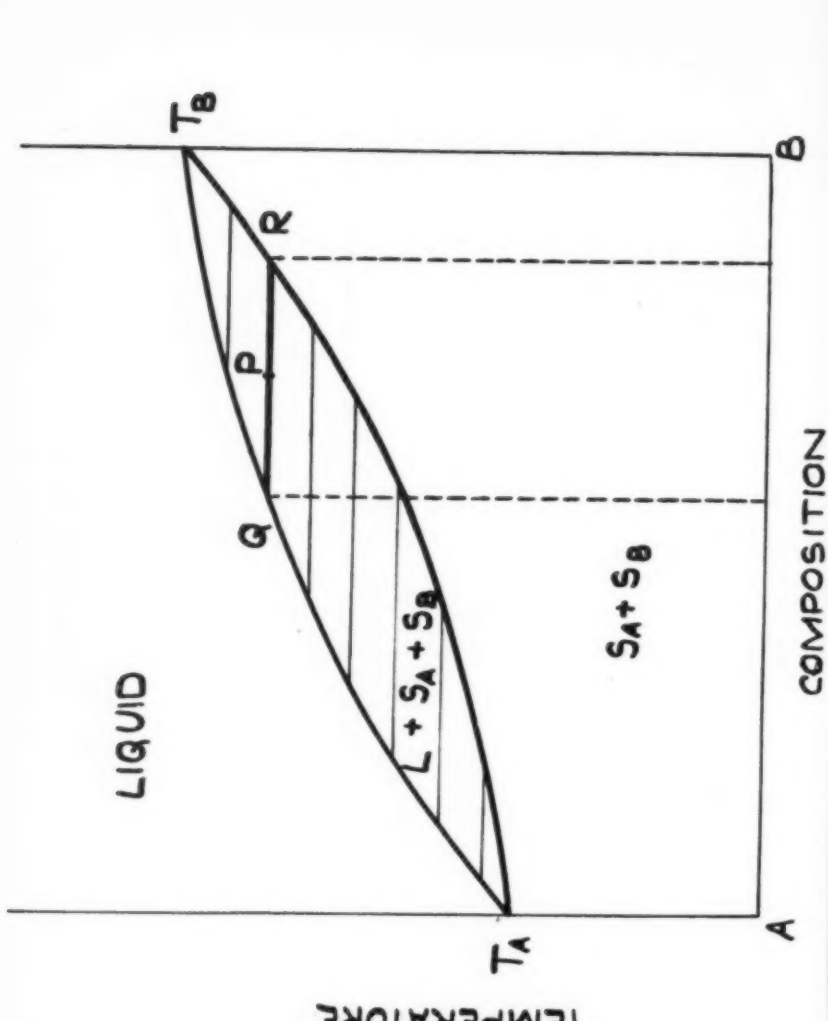

$T_B$
R
F
B
P
Q
$L + S_B$
$S_A + S_B$
LIQUID
E
$L + S_A$
$T_A$
D
A
TEMPERATURE
COMPOSITION

FIG. 1.


$T_B$
B
R
P
Q
LIQUID
$L + S_A + S_B$
$S_A + S_B$
COMPOSITION
$T_A$
A
TEMPERATURE

At point $E$ identity of composition is reached in the two liquid mixtures, so that at this point, called the eutectic point, solid $A$ and solid $B$ must exist in equilibrium with a single solution of composition $E$. The horizontal line $DEF$ is the lower boundary of the liquid–solid areas $T_ADE$ and $T_BFE$, and below it only solid can exist.

Another type of equilibrium between $A$ and $B$ is shown in Fig. 2. In this case the addition of $B$ to the melt of pure $A$ raises the temperature of equilibrium between solid and liquid. Further, a liquid mixture of $A$ and $B$ is in equilibrium with a single solid phase which is a solid solution

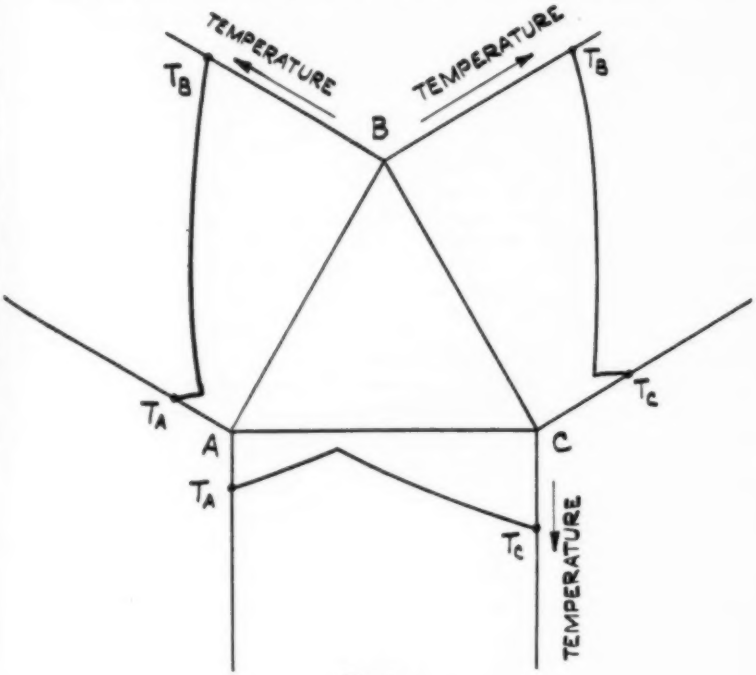



FIG. 3.

of $A$ and $B$. The composition represented by a point $P$ now separates into liquid of composition $Q$ and a single solid phase of composition $R$. The curves $T_AQT_B$ and $T_ART_B$ are the freezing-point and melting-point curves respectively for the system $AB$.

Each of the three binary mixtures $AB$, $BC$ and $CA$, making up the ternary system $ABC$, may be one or other of the two equilibrium types described above. The three binary equilibrium systems may then be attached to the sides of an equilateral triangle as in Fig. 3, and the equilibrium of the ternary system at any given temperature represented within the triangle $ABC$.

By folding along $AB$, $BC$ and $CA$ in Fig. 3 a solid prismatic figure

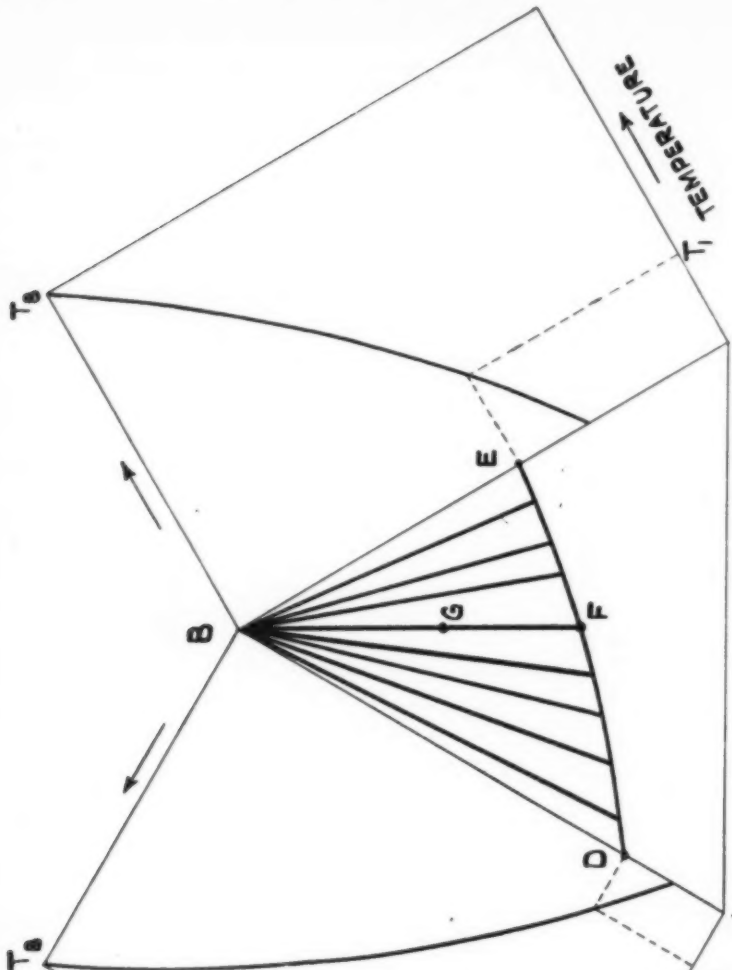



FIG. 4.

would be obtained with *ABC* remaining in the horizontal plane and the temperature axes situated vertically above *A*, *B* and *C*. The equilibrium at any temperature for the ternary system would then be represented by a surface within the prism.

In Fig. 4 equilibrium in the ternary system *ABC* is represented in the triangle *ABC* at temperature $T_1$. Attached to the two sides *AB* and *CB* of the triangle are representations of equilibrium in the two binary systems *AB* and *CB*. These two binary systems are of the type shown in Fig. 1, but the temperature range has been restricted to such limits that only component *B* appears in the solid phase. On the side *CB* of the triangle point *E* represents the composition of the liquid phase (a mixture of *B* and *C*) in equilibrium with solid *B* at temperature $T_1$. Similarly, point *D* on the side *AB* represents the composition of the liquid phase (a mixture of *A* and *B*) in equilibrium with solid *B*. Point *F* represents the composition of a liquid phase, which is a mixture of *A*, *B* and *C*, in equilibrium with solid *B*. The lines *BD*, *BF* and *BE* are tie-lines. Any mixture of *A*, *B* and *C* at temperature $T_1$ the composition of which can be represented by a point within the area *BDFE* must exist as two phases, a solid phase *B* in equilibrium with a liquid phase which has a composition represented by a point on the curve *DFE*. For example, a mixture of composition *G* at temperature $T_1$ will exist as a solid–liquid system consisting of solid *B* in equilibrium with a liquid of composition *F*. The ratio of solid phase *B* to liquid phase of composition *F* will be the ratio of the length *GF* to the length *GB*. All mixtures the compositions of which can be represented by a point within the area *ADFEC* will exist at temperature $T_1$ as a single liquid phase. The equilibrium in the ternary system *ABC* at temperature $T_1$, where one component, *B*, is a solid and two components, *A* and *C*, are liquids, is represented by the equilibrium or solubility curve *DFE* and the tie-lines on the triangular diagram. Since all tie-lines pass through an apex of the triangle, they are usually omitted on the triangular equilibrium diagram.

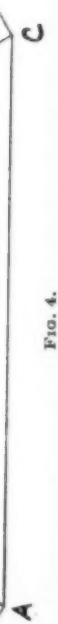


FIG. 4.

## OIL–WAX–SOLVENT EQUILIBRIA.

An approximate representation of equilibrium in an oil–wax–solvent system may be obtained by assuming the oil and the wax each to be a single pure component. Since oil and wax are complicated liquid and solid solutions of hydrocarbons, this assumption introduces certain quantitative inaccuracies into any equilibrium representation based upon it. Exact quantitative representation of equilibrium in an oil–wax–solvent system can be obtained by the use of solid geometrical figures. Such methods are, however, rather complicated, and clumsy in use. The employment of graphical representation on a single plane made available by the above assumption has many advantages, which more than offset any slight loss of accuracy, the actual quantitative error involved being small and of little importance in technical calculations and interpretations.

A necessary condition of the dewaxing process is that the diluent or solvent and the oil be completely miscible and liquid at the operating temperature. The lowest temperature to be considered, therefore, must be higher than both the freezing point of the oil and the freezing point

of the solvent. These temperature considerations restrict the ternary equilibrium isotherm to the simpler case already discussed and illustrated in Fig. 4. The three components $A$, $B$ and $C$ of this figure may now be replaced by the three components oil, wax and solvent or diluent. The resulting equilibrium diagram for this system is shown in Fig. 5. Since the oil–solvent mixtures are totally liquid over the temperature range in question, there is no solid–liquid equilibrium curve attached to the oil–solvent composition side of the triangle. Only those portions of the oil–wax and solvent–wax equilibrium curves embracing the cooling range of temperatures are required, and these portions are, again, above the freezing points of pure oil and pure solvent, and hence also above the eutectic points of the oil–wax and solvent–wax mixtures if such exist.

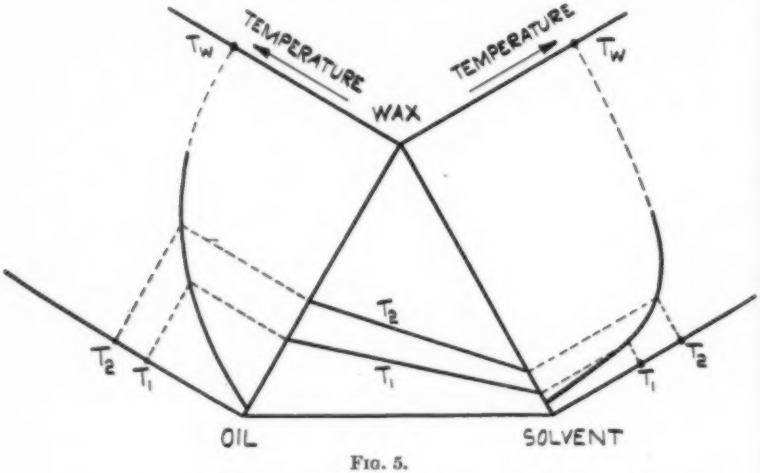



FIG. 5.

The rectangular co-ordinate portions of Fig. 5 therefore show the solubility curves of wax in pure oil and in pure solvent over the required temperature range. From these two curves the terminal points of the equilibrium curves on the ternary diagram are obtained. Intermediate points in the triangle can be obtained from the solubility curves of wax in different oil–solvent mixtures. In the case, for example, of a 1 : 1 solvent–oil mixture the rectangular co-ordinate graph containing the solubility curve of wax in this mixture would be attached to the line joining the apex representing pure wax to the mid-point of the oil–solvent composition line. In this way the isothermal equilibrium line at any required temperature may be constructed. Two isothermal lines are shown in Fig. 5 at temperatures $T_1$ and $T_2$.

Fig. 6 is a representation of equilibrium data for an oil–wax–solvent system giving the temperature variable. This takes the form of a solid prismatic figure with the temperature variable along the vertical axis. The shaded portion of the prism represents the solid–liquid region of the

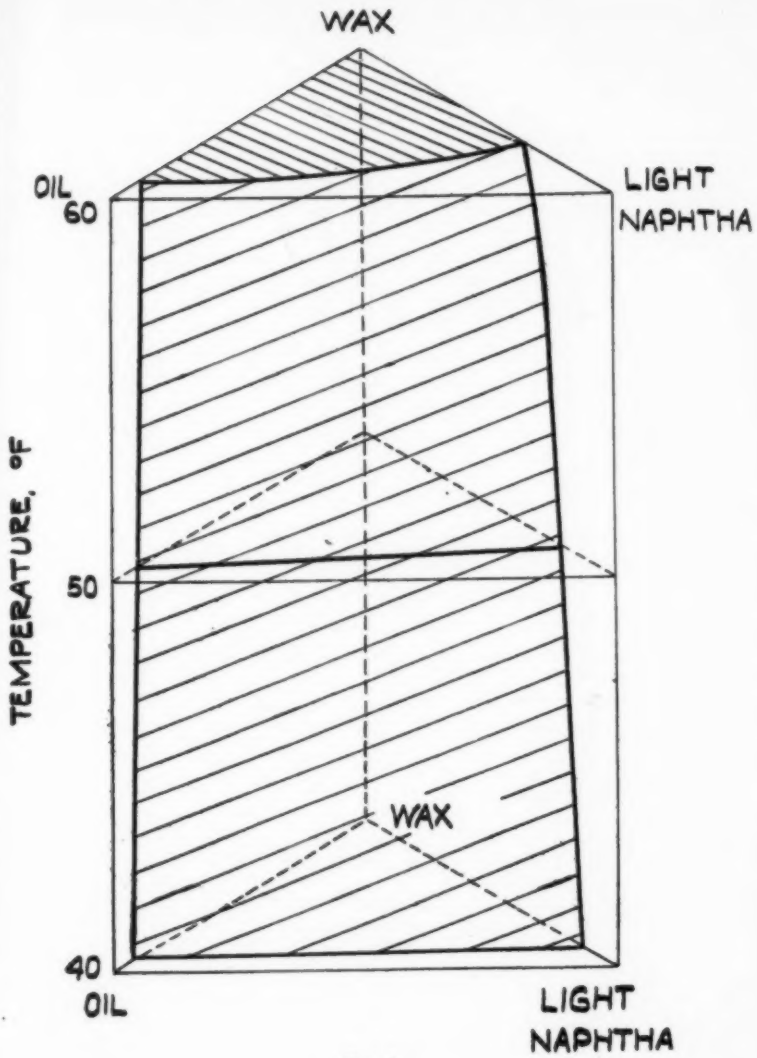



FIG. 6.

system, and the unshaded portion the completely liquid region. Projection of the solid surface at any temperature plane on to the triangular base produces the isothermal solubility curve on the triangular diagram. Fig. 6 is a reproduction of actual equilibrium data for the system lubricating oil–paraffin wax–light naphtha over the temperature range 40–60° F.

Fig. 7 shows the complete representation of an oil–wax–solvent system. On to the ternary diagram, in which is drawn the equilibrium curve $XY$ for the system at a given temperature $t°$ F., are attached rectangular co-ordinates, linked to the oil–wax composition line of the triangle. The oil–wax composition side of the triangle is also the abscissa of the rectangular co-ordinates, of which the ordinate represents temperature. The two scales of the attached rectangular co-ordinates are therefore oil–wax composition and temperature. On these scales is plotted the pour point of varying oil–wax mixtures, shown in Fig. 7 as the oil–wax pour-point curve, and also the melting point of varying oil–wax mixtures, shonn in the figure as the oil–wax melting-point curve. In this particular form the diagram is most useful for dewaxing calculations.

As mentioned above, this method of representation is not completely quantitative. Over the temperature range used in dewaxing only two phases exist, liquid and solid. Under these conditions the liquid phase must vary between wax-free oil + solvent and wax + oil + solvent. Therefore, as long as temperature conditions are such that only one liquid phase is present, the oil may be treated as if it were a single pure component, since the total oil present in the system will always be in the liquid phase. The original assumption then introduces no error in this connection. Over the specified temperature range, the solid phase will be wax varying in amount with varying temperature and solvent conditions. The total wax present in the system will thus be divided between the two phases, with varying amounts in the solid phase and in the liquid phase, depending on conditions. Since wax is a complex solid solution or solid mixture of hydrocarbons, the composition of the solid wax phase and the composition of the wax dissolved in the liquid phase must vary with varying conditions. This variation in composition of the wax could be represented quantitatively by some characteristic physical property such as melting point. If on Fig. 7 the melting point of the pure solid phase could be shown, then the equilibrium representation would be quantitatively exact. In order to do this, Fig. 7 would have to be replaced by a solid figure.

## Dewaxing Computations.

Fig. 7 may be used for graphical computations on dewaxing operations. For example, suppose a lubricating oil stock with a pour point of 73° F. is to be dewaxed with the addition of a solvent or diluent by chilling to and filtering at $t°$ F. The ratio of solvent to stock to be used in the process is $R$. Suppose also that the filtering process gives a cake of melting point 104° F., consisting of wax and mechanically entrained oil. What is the yield of solvent-free cake and dewaxed oil? What is the percentage of oil in the solvent-free cake, and what is the pour point of the solvent-free dewaxed oil? What percentage of solvent is present in the cake and filtrate obtained from the process? If the curve $XY$ of Fig. 7 represents the equilibrium between wax-free oil, paraffin wax and solvent—at the dewaxing temperature $t°$ F., then this figure can be used as a basis for computing the answers to these questions.

In Fig. 7 $D'$ represents the pour point of the oil stock to be dewaxed—

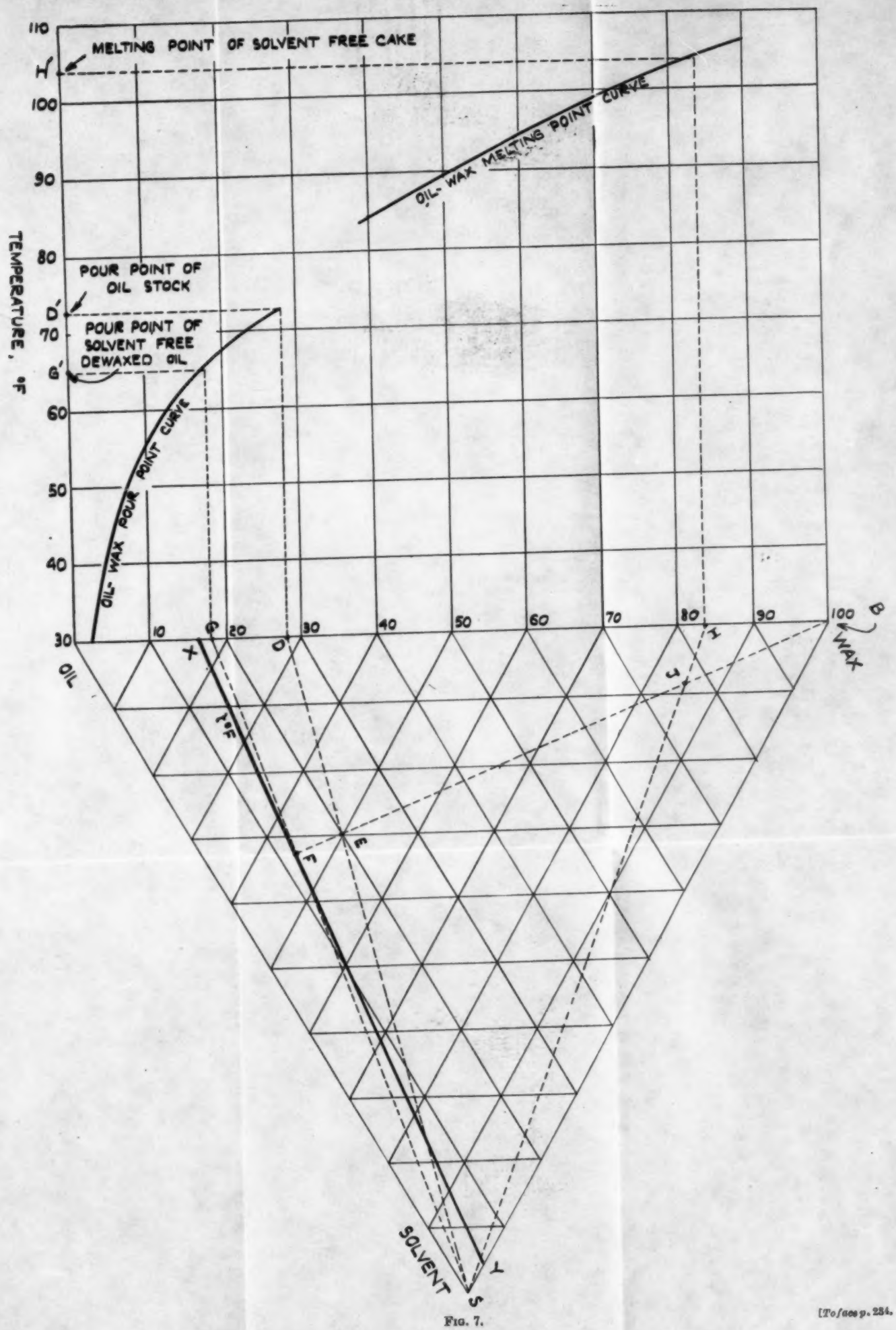



FIG. 7.

[To face p. 234.

namely, 73° F. From $D'$ by means of the wax–oil pour-point curve the point $D$, representing the percentage wax in the stock, is obtained. To the stock solvent is added, in amount such that the ratio of solvent to stock is $R$. The composition of the mixture of solvent and stock so obtained must be on the line joining point $D$, representing the composition of the stock, to the point $S$, representing the composition of the solvent. If the composition of this stock and solvent mixture is represented by point $E$, then $E$ must be located on $DS$, so that $DE/ES$ equals the required solvent/oil ratio $R$. The solvent and stock mixture, of composition represented by point $E$, is now cooled to the dewaxing temperature $t°$ F. Since $E$ lies within the two-phase solid–liquid area of the isothermal ternary diagram, the stock and solvent mixture must exist as two phases : a solid phase and a liquid phase. The composition of these two phases must be located by the tie-line passing through the point $E$—that is, by the line $FEB$. The point $B$ then represents the composition of the solid phase—namely, wax—while $F$ represents the composition of the liquid phase, a solution consisting of wax, oil and solvent. The ratio of the solid to the liquid phase will be equal to the ratio $EF/EB$.

The cake obtained on filtration consists of the solid phase, wax, together with mechanically held liquid. This liquid must have the composition indicated by $F$. Therefore the composition of the cake, a mixture of the solid phase and mechanically held liquid phase, obtained on filtration before solvent is removed from it must be somewhere on the line $FB$. The melting point of the solvent-free cake is 104° F. and the composition of the solvent-free cake can be taken as the composition of the wax–oil mixture having this melting point. From the melting point, $H'$, of the solvent-free cake and from the wax–oil melting-point curve the composition of the solvent-free cake in terms of oil and wax is located as point $H$. The composition of the cake obtained on filtration before the solvent is removed must therefore also lie on the line joining the point representing the composition of the solvent-free cake $H$ and the point representing the composition of the solvent $S$. The intersection of $HS$ and $FB$ at $J$ must represent the composition of the cake obtained on filtration before solvent removal. The yields of actual cake and filtrate can then be obtained from the ratio $EF/EJ$, which is the ratio of cake to filtrate. The percentages of solvent in both the cake and the filtrate can be read directly from points $J$ and $F$ respectively.

The composition of the dewaxed oil after freeing from solvent must lie on the straight line passing through $F$ and $S$, and must be the point on this line where the solvent concentration is zero—that is, where it cuts the left-hand side of the triangle, namely, point $G$. The pour point of the dewaxed oil is then easily read from the oil–wax pour-point curve as $G'$ equal to 65° F. in Fig. 7. The final yield of solvent-free cake of melting point 104° F. and dewaxed oil of pour point 65° F. are obtained from the relationship $DG/DH$ equal to the ratio of solvent-free cake to dewaxed oil.

The equilibrium diagram can be used in the above way for computing the results to be obtained from a dewaxing operation, provided that either the melting point of the solvent-free cake or the amount of oil in the solvent-free cake is known. Since the oil present in the solvent-free cake

is oil mechanically retained during the filtering operation, the cake melting point must be entirely determined by the filtration method and equipment employed, and its value and variation could be easily obtained for a given piece of equipment as a function of operating conditions. It is possible that some of the oil present in the cake may be actually dissolved in the solid wax. If this was so, the solid phase at equilibrium would be, not wax, but a solid solution of oil or oil and solvent in wax. In such a case the equilibrium diagram would differ somewhat from that shown in Fig. 7, but computations would still be possible. In all the instances examined experimentally by us no evidence for the existence of a solid solution of oil, solvent, or oil and solvent in wax was obtained, and it is believed that the possible occurrence of such solid solutions is remote.

### Experimental Determination of the Equilibrium Diagram.

Experimental data for the construction of equilibrium diagrams may be obtained by either a direct or an indirect method. Since the yield and character of the dewaxed oil, obtained in the dewaxing process, sometimes depend to some extent on the rate of chilling and on the length of time the chilled mixture is held at the dewaxing temperature, a direct method is usually more satisfactory. In a direct method the data used for constructing the equilibrium diagram must be obtained by small-scale dewaxing experiments. These experiments most conveniently consist of filtration experiments carried out, at chilling rates and time at dewaxing temperature, identical with the rates and time employed under the proposed working conditions. The equilibrium line at any one particular temperature, $t°$ F., can then be plotted from the results of three, or more accurately from four, determinations. These experiments are: first, filtration of the wax-bearing stock at $t°$ F.; second and third, filtrations at $t°$ F. of wax-bearing stock with known suitable amounts of solvent added; fourth, filtration of a suitable mixture of solvent and wax at $t°$ F. Analysis of the filtrates obtained gives sufficient information to construct the equilibrium diagram at $t°$ F. for the particular wax-bearing stock and solvent used. Since the equilibrium curve represents the composition of the liquid phase in equilibrium with the solid phase—wax—only analysis of the liquid phase—filtrate—is required. The pour point of the filtrate from the first filtration, the per cent. solvent in the filtrate and the pour point of the solvent-free oil from the second and third filtrations, and the per cent. wax in the fourth filtrate are the only analytical data required. By the use of an oil–wax pour-point curve, attached to the side of the triangular diagram as in Fig. 7, these data can be plotted on the triangular diagram to produce the required equilibrium curve. The oil–wax pour-point and the wax–oil melting-point curves are best constructed from synthetic mixtures of previously separated oil and wax. Care has to be taken that the previously separated wax used is representative of the bulk of the wax present in the oil. The pour-point and the melting-point curves are used, of course, for all equilibrium diagrams pertaining to one wax-bearing stock at all dewaxing temperatures. In all the cases so far examined by us the oil–wax pour-point curve has been found to be a straight line when pour point is plotted against log oil–wax composition.

If this relationship is general, it is obvious that this curve could be constructed from two or three points only, provided the extrapolated range was not too extensive. In carrying out pour-point determinations it must be emphasized that the standard method of determination, where the pour tube is inverted every 5° F., is not sufficiently accurate for this type of work. Using the standard method the error varies from + 1° to + 4° F. In the construction of and in computations based on the equilibrium diagram the pour-point curve is used as a measure of wax content, and since an error of + 4° F. in the pour point represents an error in wax

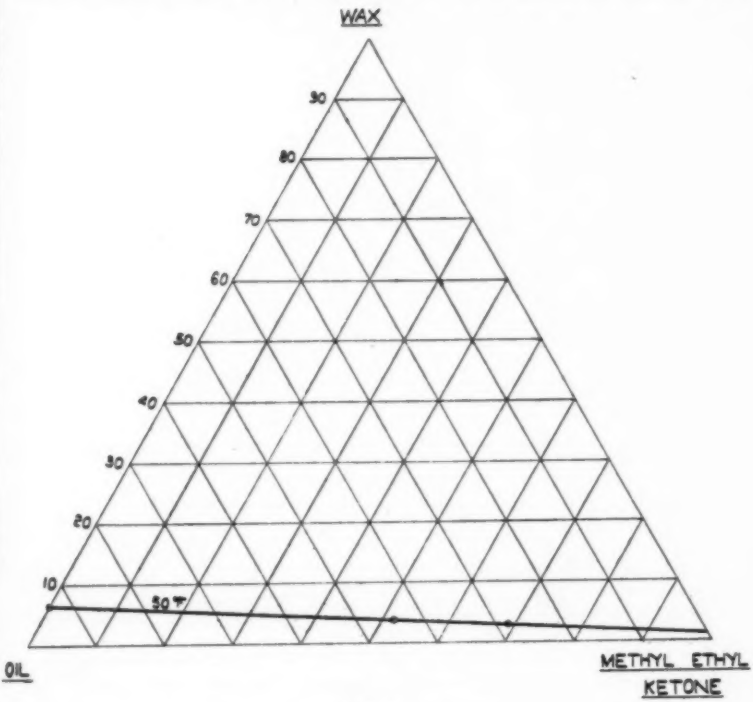



FIG. 8.

content of from about + 20 per cent., pour points should therefore be determined correct to within 1° F.

In Fig. 8 the equilibrium diagram for a wax-free Iranian lub. oil fraction and a paraffin wax, melting point 108° F., with methyl ethyl ketone as a solvent, at 50° F. is illustrated. This diagram was constructed from the data obtained from three filtration experiments as described above. In Fig. 9 the equilibrium curves at temperatures of 40°, 50° and 60° F. for the same oil and wax but with amyl alcohol as a solvent are shown. As in Fig. 8, these were obtained by direct filtration experiments. Carlisle and Levine [7] describe the dewaxing of a wax

distillate with methylene chloride. From their dewaxing data at a chilling temperature of — 13° F., using a chilling rate of 18° F./hour, with a standing time of 1 hour, Fig. 10 has been constructed. These investigators tabulate data for dewaxing with four different solvent–oil ratios. This data gave the four points on Fig. 10 joined to the apex by the broken constructional lines. Of the remaining two points in the figure one was obtained from the data given in the paper on the solubility of wax in methylene chloride at — 13° F., while the other was obtained by extra-

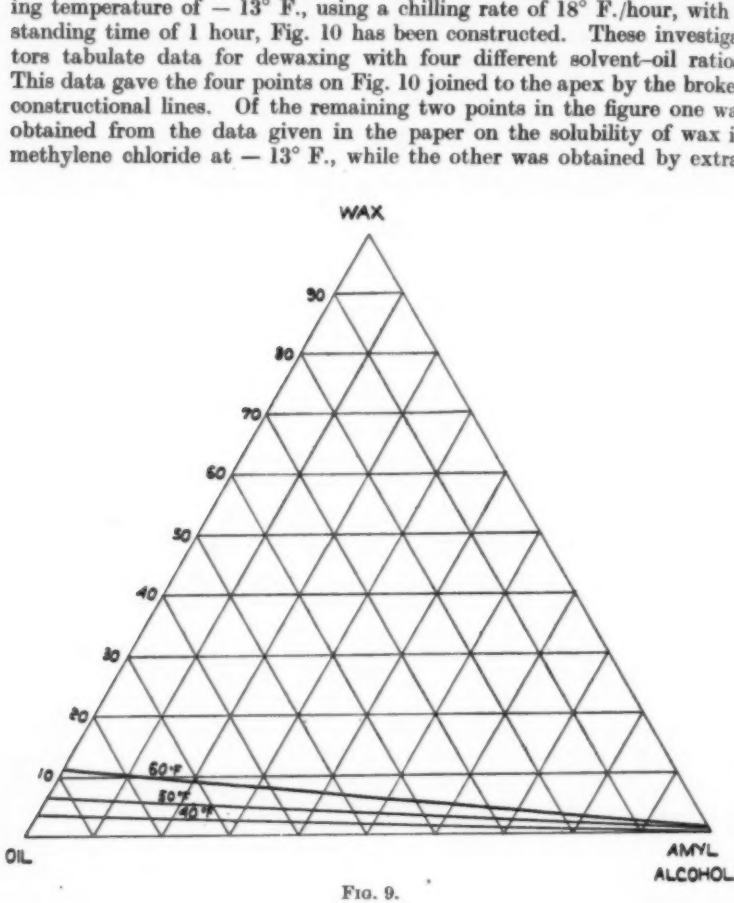



FIG. 9.

polation. The equilibrium curves for all the above three solvents are straight lines at the prevailing temperatures.

The equilibrium curve in the ternary diagram is actually a solubility curve representing the solubility of wax in oil, in oil–solvent mixtures and in pure solvent at the prevailing temperature. A point on this solubility curve represents the composition of the binary or ternary mixture which at the equilibrium temperature is saturated with wax. An unsaturated ternary solution at a temperature $t_2$ if cooled to a temperature, say $t_1$, at which it is saturated, still remains a homogeneous solution. If it is further cooled, a fraction of a degree below $t_1$ the solution becomes supersaturated, and tends to attain equilibrium by depositing wax as a

solid phase. Cooling a solution of wax, oil and solvent of known composition down to a temperature $t$ where the solution becomes cloudy due to appearance of solid wax, means that at temperature $t$ the solution of original known composition is in equilibrium with the solid wax phase. That is, the original known composition of the solution must represent a point on the isothermal solubility curve for the ternary system wax–oil–solvent at temperature $t$. Therefore, determining the cloud point of a solution of oil, wax and solvent of known composition is sufficient to locate a point (the known composition of the solution) on the solubility curve at an equilibrium temperature equal to the cloud-point tempera-

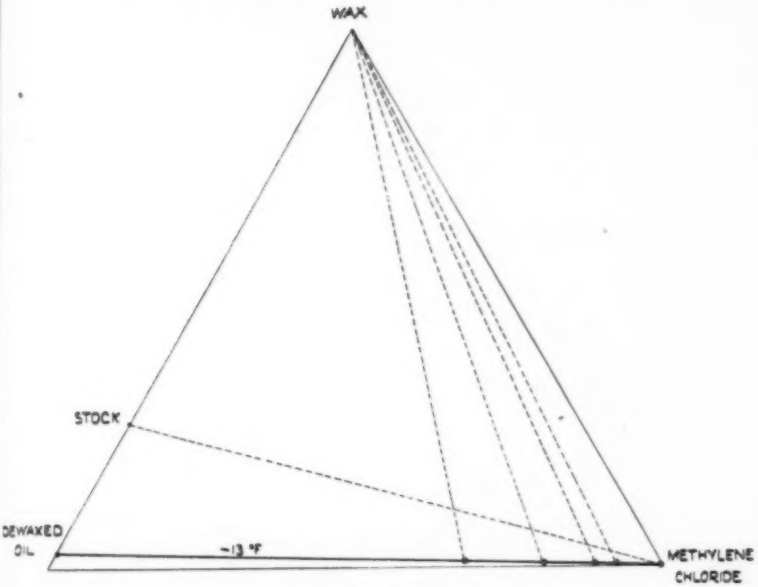



FIG. 10.

ture. Given three different wax–oil–solvent mixtures all of known composition and all with a cloud point $t$, then the three points on a ternary diagram, representing the three known compositions, must be three points lying on the isothermal solubility curve for the wax–oil–solvent system at temperature $t$. It is obvious therefore that an easy indirect method of constructing the equilibrium curve is by ordinary cloud-point determinations on known synthetic mixtures. Fig. 11 shows the equilibrium curves for three temperatures for the system Iranian lub. oil, wax of melting point 108° F. and light naphtha, boiling range 100–120° C. These curves were constructed entirely from ordinary cloud-point determinations.

The cloud-point method of obtaining the equilibrium diagram is obviously a convenient and easy one. It possesses, however, one grave disadvantage, in that when employed with certain solvents it is inaccurate. For a

system of three pure components data obtained from cloud-point or, more usually termed for this case, freezing-point determinations are, of course, entirely reliable. For a system where the solid phase consists of a large number of components, like paraffix wax, unavoidable errors are introduced by the use of cloud points, particularly for certain solvents. For example, on cooling a single homogeneous solution of composition, say, 10, 50 and 40 per cent. wax, oil and solvent respectively, in a cloud-point determination, the solid phase would appear at, say, 50° F. This result, in the usual way would be taken to mean that a liquid of composition 10, 50 and 40 per cent. wax, oil and solvent was in equilibrium with solid wax at 50° F.

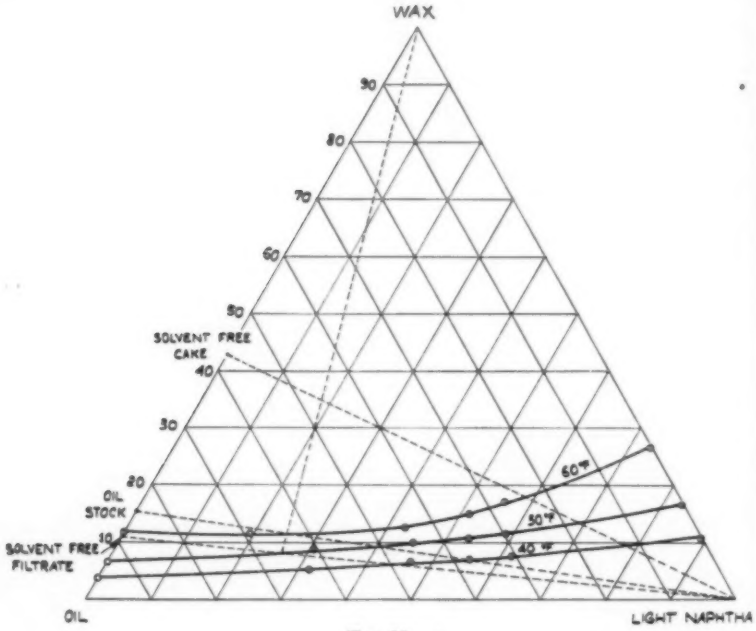



FIG. 11.

When checked by the direct filtration method, however, equilibrium between a liquid of this composition and solid wax would be found to occur at a lower temperature, say, 45° F. By filtration the liquid phase in equilibrium with solid wax at 50° F. would be found to be not 10, 50 and 40 per cent. wax, oil, solvent, but 15, 45 and 40 per cent. wax, oil, solvent. That is, at 50° F. the cloud-point method gives a wax solubility of 10 per cent., whereas 15 per cent. is obtained by the filtration method. Wax is, of course, a mixture of a large number of components, all of different solubility in the solvent, some being more and others less soluble. Since wax is being considered as a single substance, the average solubility of the wax as a whole is the solubility desired and is the solubility obtained by the filtration method.

In the cloud-point determination the first solid phase to appear consists mainly of the least-soluble components of the wax, and hence this method gives not the average solubility of the wax as a whole, but the solubility of the less-soluble constituents. The less-soluble components of the wax possess higher melting points than the more soluble components. A solvent from which the wax crystallizes in the form of a solid with a much higher melting point than the original wax therefore tends to give erroneous solubility data when the equilibrium is determined by the cloud-point method. Such a solvent is amyl alcohol, from which, for example, wax

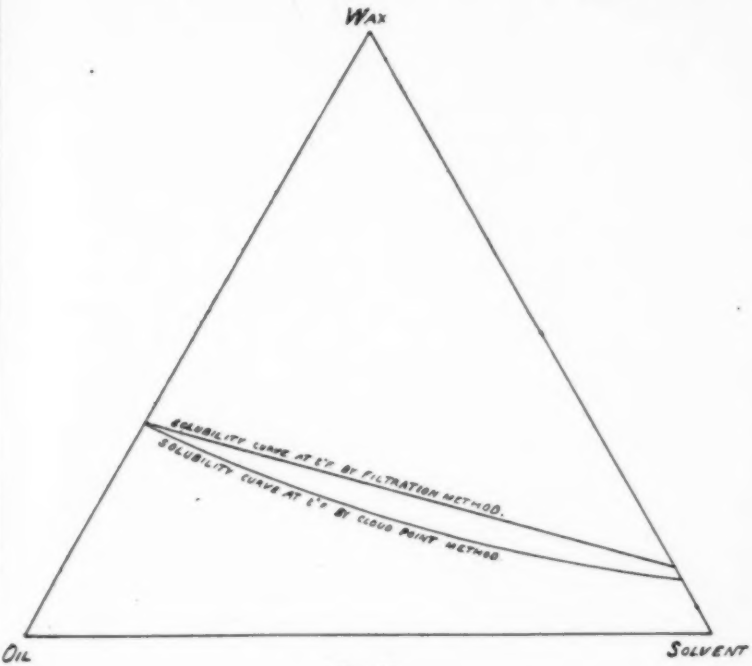



FIG. 12.

of original melting point 108° F. was found to crystallize as wax of melting point 126° F. The two different solubility curves obtained from such a solvent at temperature $t$° F. using the filtration and cloud-point methods are shown in Fig. 12. For the purposes of illustration, the difference between the two curves has been exaggerated in the figure. It will be seen that when no solvent is present the data obtained from both the cloud-point and the filtration methods agree. With increasing amounts of solvent the cloud-point solubilities are increasingly lower than the filtration solubilities up to a point where, on still further increasing the amount of solvent in the mixture, the two lines begin to approach each other. When the wax–solvent binary mixture is reached, the error in

the solubility measured by the cloud point is large compared with the actual solubility, which is small here. The data obtained from filtration experiments fall on a straight line, whilst those from cloud-point determinations fall on a slight curve. Sullivan, McGill and French [13] have found that difference of solubility due to difference of melting point decreases with decreasing temperature, so that it is highly probable that

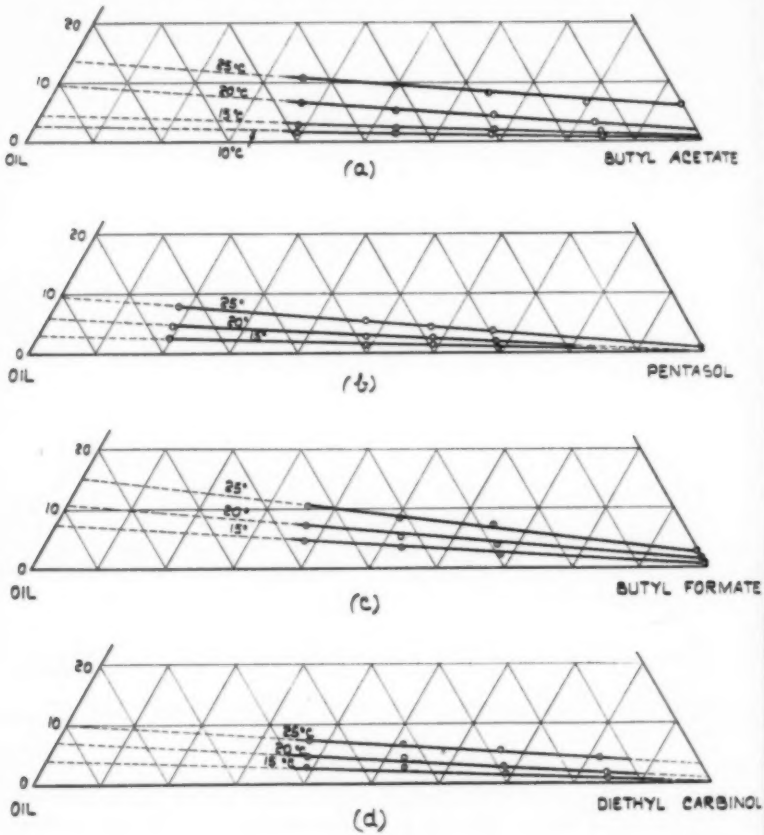



FIG. 13.

at low temperatures both methods would give identical results. In the case of a solvent in which the difference in solubility between the high and low melting-point waxes is not pronounced, the cloud-point method may be used with success for determining solubility data. The light naphtha used for the equilibrium data of Fig. 11 is such a solvent.

Another method of determining solubility data is that employed by Poole.[8] This method is very convenient, and is free from the error some-

times introduced by certain solvents into the cloud-point method. In this method a known mixture of oil and solvent is placed in a test tube and excess wax added. The whole is kept at the desired temperature for a period of about 12 hours. At the end of this time both liquid and solid phases must be present, the solid phase in fair amount. Some of the liquid phase is then removed and its composition ascertained by analysis. Various liquid phase compositions at constant temperature give the isothermal solubility curve on the ternary diagram. This method is accurate provided sufficient wax is present in the solid phase to be representative of the wax as a whole.

Poole [8, 9, 10] in three papers has published solubility data determined by the above method for paraffin wax, melting point 50° C., in various solvents and solvent–oil mixtures at different temperatures, using as the oil two Pennsylvanian paraffin-base lub. oils. Poole's data for four solvents, butyl acetate, butyl formate, pentasol and diethyl carbinol, have been recalculated and plotted on ternary diagrams in Fig. 13. The equilibrium lines obtained from Poole's experiments are incomplete owing to the fact that he did not determine the solubility of the wax in the oils used.

For all solvents so far examined by us the solubility curves when plotted on the triangular diagram are straight lines. The one exception is light naphtha, used as a solvent at temperatures higher than 60° F., and the deviation from a straight line in this instance would appear to be due to the high equilibrium temperature, which is much higher than any likely to be employed in actual dewaxing practice. If all such equilibrium curves at low temperatures proved to be straight lines, or curves deviating very slightly from straight lines, then the following very easy method of constructing the ternary equilibrium solubility diagram could be used. One terminal point of the solubility curve at a given temperature could be easily obtained from cloud-point determinations on oil–wax mixtures or from one solubility determination of wax in oil at the required temperature using Poole's method. The other terminal point could be determined from one solubility measurement of wax in solvent at the required temperature also by Poole's method. Merely connecting these two points on the ternary diagram by a straight line would then complete the data.

## Classification of Solvents.

The ternary equilibrium diagrams form a sound basis for the classification and comparison of dewaxing solvents. The first essential feature of a solvent is that it must be completely miscible with the oil at the dewaxing temperature. All known solvents of this type fall into four classes :—

(I) *Solvents which possess a greater solvent power for wax than does the wax-free hydrocarbon oil.* Solvents in this class exhibit a solubility curve, such as *A* or *B* in Fig. 14. When such solvents are employed in a dewaxing process the pour point of the dewaxed oil obtained increases with increasing solvent–oil ratio. The pour point of the dewaxed oil obtained without the use of a solvent is always lower than

that obtained at any similar temperature when such solvents are used. Light naphtha is a typical solvent of this class giving solubility curves similar to *A* at 40° F. and to *B* at 60° F.

(II) *Solvents in which the wax is negligibly soluble, totally insoluble, or in which the wax, although appreciably soluble, is less soluble than it is in the wax-free oil.* An equilibrium curve like *C* in Fig. 14 is characteristic of this class of solvents. Alteration of the solvent–oil ratio when dewaxing with solvents in which the wax is negligibly soluble or totally insoluble has either very little or no effect on the pour point

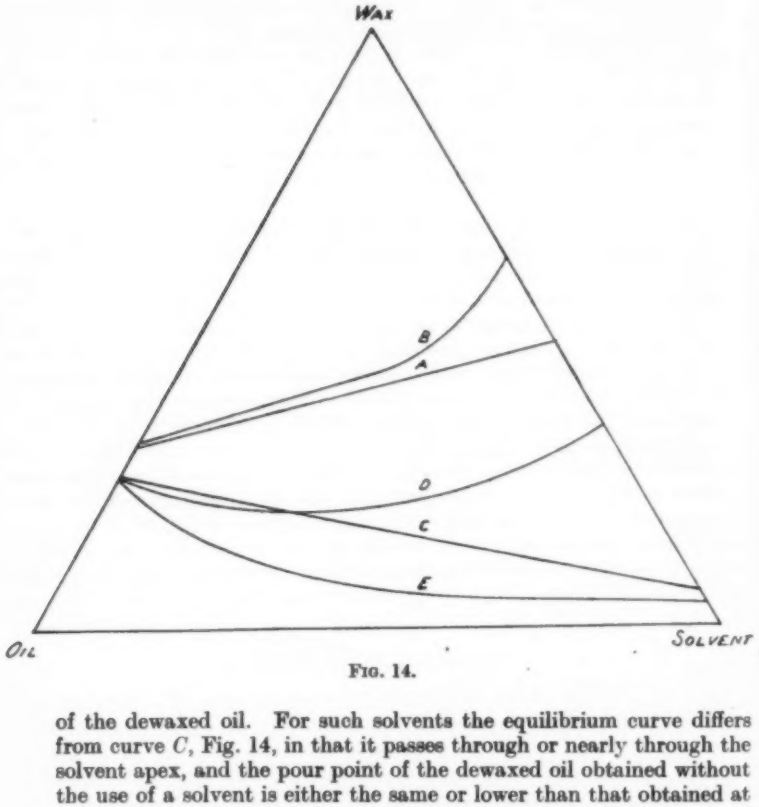



FIG. 14.

of the dewaxed oil. For such solvents the equilibrium curve differs from curve *C*, Fig. 14, in that it passes through or nearly through the solvent apex, and the pour point of the dewaxed oil obtained without the use of a solvent is either the same or lower than that obtained at any similar temperature when such solvents are used. For solvents of this class in which the wax is appreciably soluble, but still of course less soluble than in the wax-free oil, then the pour point of the dewaxed oil increases with increasing solvent–oil ratio, while the pour point of the dewaxed oil obtained without the use of a solvent is lower than that obtained at any similar temperature when such solvents are used.

A typical solvent in this class is amyl alcohol.

(III) *Solvents which, when added to an oil–wax mixture, at a given temperature, first precipitate wax and then on the addition of more solvent redissolve part or all of the precipitated wax.* These solvents give an equilibrium curve like *D*. When used for dewaxing, an increase in the solvent–oil ratio up to a certain point decreases the pour point of the dewaxed oil. Any increase in the solvent–oil ratio above this point increases the pour point of the dewaxed oil. The pour point of the dewaxed oil obtained without the use of a solvent would always be higher than the pour point obtained using such solvents up to the critical solvent–oil ratio, whilst at a ratio above the critical ratio the pour point of the dewaxed oil is always higher than that obtained when no solvent is used.

(IV) *Solvents with which the amount of wax precipitated increases and the pour point of the dewaxed oil decreases with increasing solvent–oil ratio up to a critical ratio.* A typical solubility curve for such solvents is shown by *E* in Fig. 14. The pour point of the dewaxed oil obtained by the use of such solvents up to the critical ratio is always lower than the pour point of the dewaxed oil obtained when no solvent is used.

For dewaxing processes solvents of class I are obviously the least efficient, and those of class IV, at solvent ratios below the critical ratio, the most efficient. A large majority of the solvents usually used approximate to class II solvents in which the wax is negligibly soluble or nearly insoluble. In this special type of class II solvents the best solvent–oil ratio to be employed is determined entirely by the viscosity and ease of filtration or centrifuging of the oil–wax–solvent mixture at the dewaxing temperature.

It is doubtful whether solvents of the third and fourth classes really exist. Maksorov [11] gives a list of solvents which he claims belong to classes III and IV. Most of these solvents, however, fail to fulfil the essential condition of solvents, viz., to be completely miscible with the oil at the dewaxing temperature.

Poole [8, 9, 10] has examined the solubility of wax and oil in a large number of organic solvents. Many of these solvents were only slightly miscible with oil at the usual dewaxing temperatures, and hence no further research on their possible uses in dewaxing was carried out. The most promising were examined in detail by Poole, and their equilibrium curves at several temperatures calculated from Poole's data are plotted in Fig. 13. It will be seen from this figure that all these solvents give straight lines on the ternary diagram, and at the lowest temperature examined are approaching class II solvents. Of other solvents examined by Poole butanol and to a slight extent chlorobenzene appear to belong to class III solvents at certain temperatures. With chlorobenzene deviation from a class 2 type towards a class III type solubility curve is only very slight, and may be, and probably is, due to experimental error. Below 30° C. butanol shows a limited miscibility with oil. Kalichevsky and Stagner,[12] discussing Poole's results, state that these " solvents are especially promising because when added in small proportions to the oils they greatly decrease the capacity of the oils to retain their dissolved wax."

As seen from Fig. 14, this statement is incorrect. The evidence that

any solvent when added to an oil–wax mixture actually precipitates wax is extremely slight, and any tendency to do so is small and apparently within the limits of experimental error for all oil-miscible solvents so far investigated.

The classification of all solvents examined by us and which are completely miscible with the oil at the dewaxing temperature is given in Table I below. As the solubility of the wax not only in the solvent but also in the oil at the particular temperature used determines the behaviour of a solvent in dewaxing this classification of these solvents pertains only to the particular temperature conditions and for the particular oil stocks mentioned in this paper.

TABLE I.

*Classification of Oil-Soluble Dewaxing Solvents.*

| Class I. | Class II. | Class III. | Class IV. |
|---|---|---|---|
| Naphtha. | Amyl alcohol.<br>Diethyl carbinol.<br>Methyl ethyl ketone.<br>Methylene chloride.<br>Butyl acetate.<br>Butyl formate. | Chlorobenzene.<br>Butanol. | |

## COMPARISON OF CALCULATED AND EXPERIMENTAL DATA.

Computations to forecast the results to be expected by a dewaxing process at any given temperature and using any given solvent have already been described. Small-scale dewaxing operations were carried out in order to check the accuracy of the computation method.

Dewaxing experiments were performed using the apparatus shown in Fig. 15. A known weight of waxy oil in most cases of about 15 per cent. wax content with a pour point of 60° to 70° F. was placed in the cylindrical vessel and a known weight of a light napthha (b. pt. 100–120° C.) added. This mixture was stirred for about 3 hours while the temperature of the cooling bath surrounding the vessel and of the oil–wax–solvent mixture was maintained constant at the desired dewaxing temperature. The mixture was then allowed to flow through the tap at the bottom of the vessel into the filter funnel below where it was filtered. The filter funnel and its contents were surrounded by a cooling bath also carefully maintained at the dewaxing temperature. The light naphtha was then removed from the filtrate by distillation under reduced pressure, and the resultant dewaxed residual oil weighed. The pour point of the dewaxed oil was determined, and from this the percentage of wax present was obtained from an oil–wax pour-point curve.

Any material remaining in the cylindrical vessel was washed out with hot benzol into the filter funnel, where the wax all dissolved, and the solution of wax, oil, light naphtha and benzol was drawn through the filter paper into a flask, the filter paper being thoroughly washed with more hot benzol. The light naphtha and benzol were then distilled off under reduced pressure, and the weight and melting point of the residual

oil–wax cake determined. Using this apparatus and light naphtha as a solvent, several runs varying both solvent–oil ratio and dewaxing temperature were carried out. The experimental and calculated results are compared in Table II. In columns two and three the wax content and pour point of the oil stock used are given. This stock was obtained by

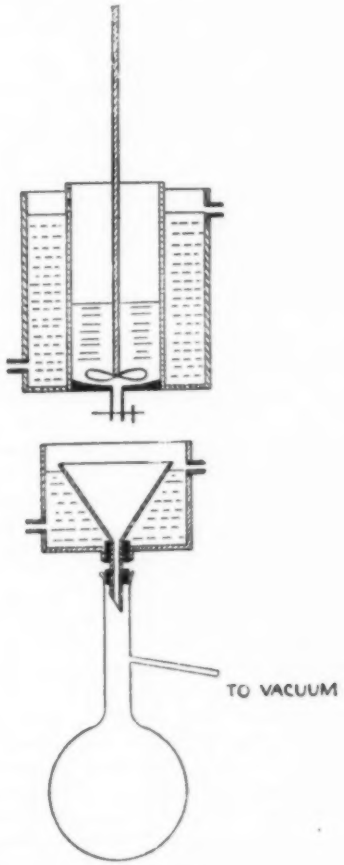



FIG. 15.

dissolving paraffin wax, melting point 108° F., in Iranian lub. oil. The solvent–oil ratio and dewaxing temperatures employed are detailed in columns three and four. In column five the melting point of the cake obtained in the experiments is tabulated. The calculated yield of cake and dewaxed oil, and the pour point of the dewaxed oil, shown in columns seven, eleven and nine respectively, were computed graphically from a

ternary equilibrium diagram, assuming the melting point of the cake was that shown in column five. The actual yields and pour point are given in columns six, eight and ten.

TABLE 11.

*Solvent : Light Naphtha (B. Pt. 100–120° C.).*

| Run No. | Oil Stock Used. | | Solvent/ Oil Ratio. | Dewaxing Temp., ° F. | Cake. | | | Dewaxed Oil. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Content Wax, %. | Pour Point, ° F. | | | Melting Point, ° F. | Yield, %. | | Pour Point, ° F. | | Yield, %. | |
| | | | | | | Actual. | Calc. | Actual. | Calc. | Actual. | Calc. |
| 1 | 54 | 91 * | 1·0 | 60 | 106 | 26·4 | 26·6 | 82·3* | 83·5 | 73·6 | 73·4 |
| 2 | 20 | 67 | 0·25 | 60 | 90 | 11·6 | 16·0 | 62 | 61 | 88·4 | 84 |
| 3 | 15 | 62 | 0·33 | 50 | 90 | 6·4 | 9·8 | 58 | 57 | 93·6 | 90·2 |
| 4 | 15 | 62 | 0·25 | 50 | 85 | 16·1 | 15·5 | 55 | 55 | 83·9 | 84·5 |
| 5 | 15 | 62 | 0·25 | 50 | 89·5 | 9·4 | 12·3 | 56 | 55 | 90·6 | 87·7 |
| 6 | 15 | 62 | 0·11 | 50 | 72 † | 38·1 | 38·1 | 50 | 51 | 61·9 | 61·9 |
| 7 | 10 | 55 | 0·25 | 40 | 82 | 12·4 | 18·4 | 46 | 45 | 87·6 | 81·6 |

* Melting point. † Pour point.

It will be seen from the table that agreement between the actual and calculated data is really excellent, considering the complicated nature of the materials handled. The equilibrium data used for the calculations are those in Fig. 11, and the dotted lines appearing in this figure are those actually used for calculating yields, etc., for run 3. The equilibrium data in Fig. 11 were constructed entirely from cloud-point determinations, which makes the agreement between the actual and calculated values still more remarkable.

These experiments were repeated using amyl alcohol and methyl ethyl ketone as solvents in place of the light naphtha.

A modified dewaxing apparatus employed for the experiments using amyl alcohol and methyl ethyl ketone as solvents is shown in Fig. 16. A filter paper and a perforated plate were fixed by means of a screw collar between a brass cylinder about 3 inches in diameter and a metal funnel, and the whole apparatus was immersed in a cooling bath. The funnel was completely filled with mercury, and the oil–wax–solvent mixture of known composition placed in the cylindrical vessel, where it was stirred for 2–3 hours. During this time the cooling bath was maintained at the desired dewaxing temperature. The stirrer was then removed, the mercury allowed to flow out, and filtration started by the application of reduced pressure below the perforated plate. After most of the mixture had been filtered the slack wax remaining on the filter paper was pressed by means of the plunger shown in Fig. 16 (*b*). By this pressing a cake of higher wax content was obtained. The pour point of the solvent-free filtrate and the melting point of the solvent-free cake were determined as before.

The experimental and calculated results are compared in Table III in the same way as before. Once again agreement is excellent. In this case the equilibrium solubility diagrams for both solvents were constructed from data obtained by the direct method. The wax and lub. oil were the

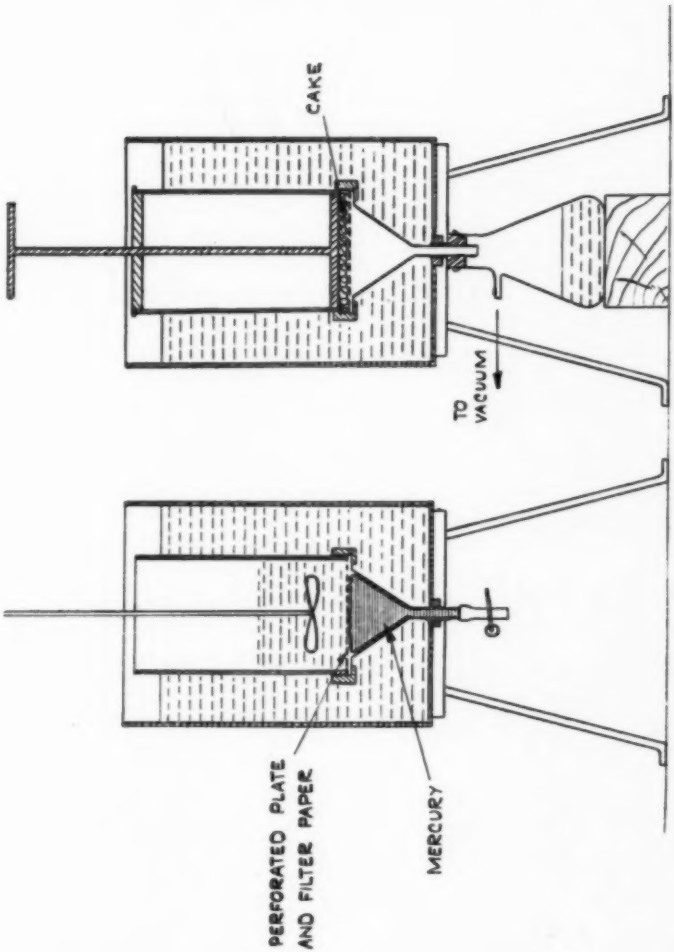

(b)
CAKE
TO VACUUM
(a)
PERFORATED PLATE AND FILTER PAPER
MERCURY

FIG. 16.

TABLE III.

| Run No. | Oil Stock Used. | | Solvent/ Oil Ratio. | Dewaxing Temp., ° F. | Cake. | | | Dewaxed Oil. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Content Wax, %. | Pour Point, ° F. | | | Melting Point, ° F. | Yield, %. | | Pour Point, ° F. | | Yield, %. | |
| | | | | | | Actual. | Calc. | Actual. | Calc. | Actual. | Calc. |
| *Solvent: Amyl Alcohol.* | | | | | | | | | | | |
| 8 | 14·6 | 61·5 | 0·83 | 50 | 74 † | 35·8 | 33·8 | 47 | 47 | 64·2 | 66·2 |
| 9 | 15·6 | 63 | 0·84 | 40 | 83 | 32·2 | 33·7 | 37 | 37 | 67·8 | 66·3 |
| 10 | 11·4 | 57 | 1·65 | 40 | 95 | 12·1 | 14·4 | 37 | 37 | 87·9 | 85·6 |
| *Solvent: Methyl Ethyl Ketone.* | | | | | | | | | | | |
| 11 | 17·9 | 65 | 0·98 | 50 | 104·25 | 8·6 | 11·4 | 51 | 51 | 91·4 | 88·6 |
| 12 | 25·9 | 72 | 1·79 | 50 | 100·1 | 26·2 | 25·1 | 52·3 | 52 | 73·8 | 74·9 |

* Melting point. † Pour point.

same as those used for the light naphtha experiments. The actual equilibrium data on which the calculations were based is shown in Figs. 8 and 9.

## COMPARISON OF DEWAXING SOLVENTS.

One of the most useful applications of the ternary diagram to dewaxing computations is for the comparison of different solvents. The effects of dewaxing temperature and solvent–oil ratio for any solvent with a given

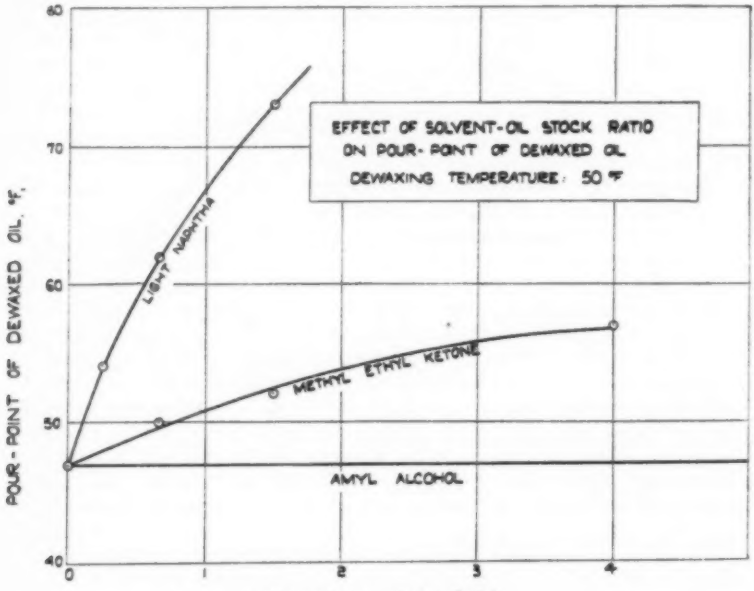



FIG. 17.

oil on yield of cake, dewaxed oil and on the pour point of the dewaxed oil are easily calculated. The efficiency of various solvents for a given oil is then readily compared on the above basis.

In Fig. 17 the pour point of the dewaxed oil obtained by using naphtha, methyl ethyl ketone and amyl alcohol for dewaxing a given

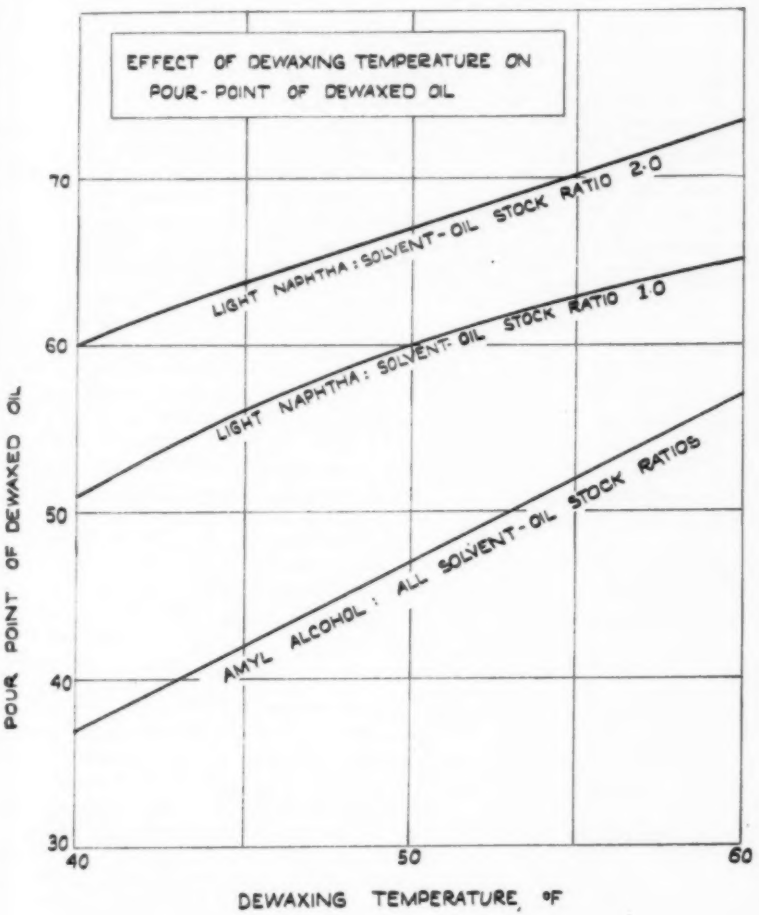



FIG. 18.

stock oil at 50° F. is compared at different solvent–oil ratios. Fig. 18 shows the effect of varying the dewaxing temperature with amyl alcohol and naphtha as solvents for the same stock oil at constant solvent–oil ratio. Comparison of solvents on these lines allows the best solvent and

the most favourable conditions to be chosen without the necessity for carrying out a large number of dewaxing experiments.

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# CONTRIBUTION TO THE KNOWLEDGE OF PHYSICAL AND CHEMICAL CONSTANTS OF GAS OILS WITH DIFFERENT CETENE NUMBERS.

By D. J. W. Kreulen (Member).

## Introduction.

Many investigators have compared the physical and chemical properties of gas oils (including the cetene number) with their behaviour in engines. The results obtained are not entirely satisfactory.

In many cases only a few properties are considered, and in none of this work is the chemical composition of the oils dealt with. Nevertheless, the "ring-analysis method" as given by Vlugter, Waterman and van Westen makes it possible to determine the percentage of aromatic and naphthenic rings, together with the percentage of paraffinic side-chains of an oil investigated.

Now, from a chemical point of view the cetene number—that is, the time elapsing between opening the fuel inlet and the commencement of rising pressure (expressed in the cetene-α-methylnaphthalene scale)—will probably be a function of the properties and quantities of the compounds of which the oil is composed. Thus it is already known that this "delay" increases in the order of sequence: paraffins, naphthenes, *iso*paraffins, aromatics. That is to say, we know that this relationship exists generally, yet how a difference in composition influences the cetene number is not known, or at least it is not published.

In this paper it is hoped to provide a contribution to the subject by giving data and analyses of eleven mineral gas oils varying in cetene number between 23½ and 65. The figures published herein are substantiated and discussed.

## Description of Methods of Analysis.

*Density.* This was determined for the original oils in a specific-gravity bottle with a volume of about 50 c.c. and for the hydrogenated oils in one with a volume of 10 c.c. The bottle with oil was held constant at 20° C. ± 0·02° C. in a water-thermostat for half an hour. The results are reliable within 0·0001 unit. Vacuum corrections were applied.

*Molecular Weight.* The cryoscopic method, using naphthalene as a solvent, was used. This method is already described by Vlugter, Waterman and van Westen (*I.P.T. Journ.*, 1935, **21**, 661).

The procedure was always such that the depression of the freezing-point was in the neighbourhood of 1° C.

It is of the greatest importance that the temperature–time curve, from which the freezing-point of the oil in naphthalene solution is derived by extrapolation, should be as accurate as possible. Therefore agitation is not effected by hand, as previous authors prescribe. An agitating mechanism was constructed which made it possible to shake automatically. For

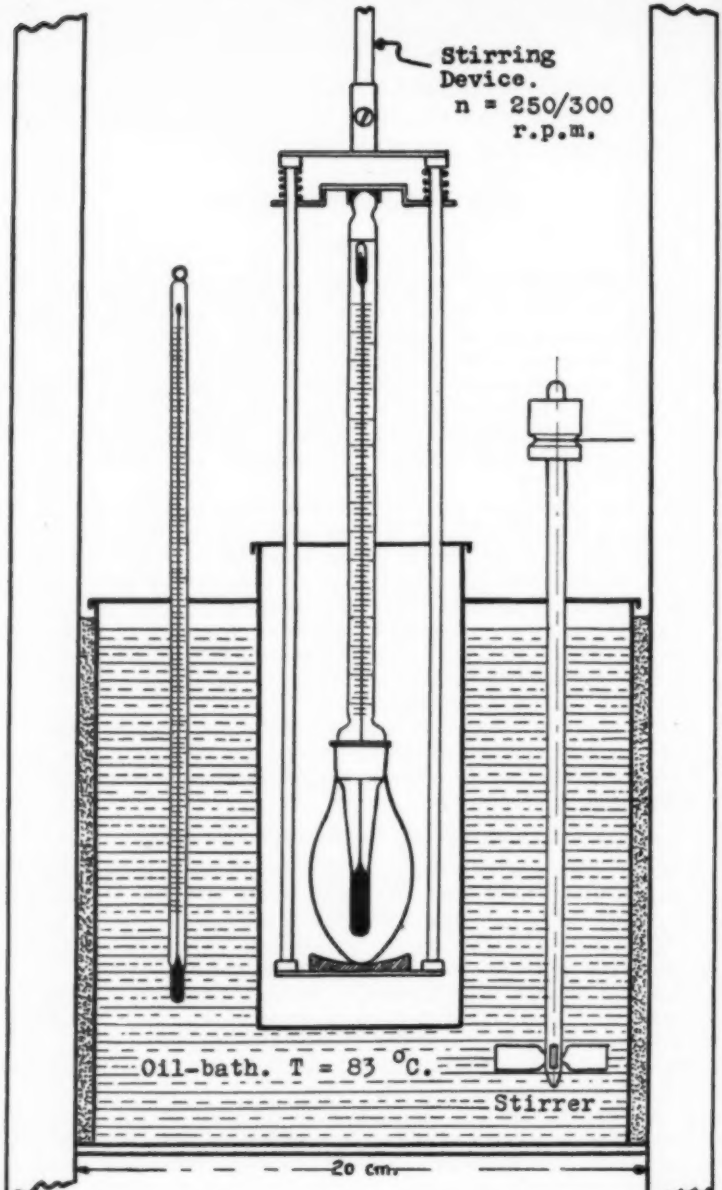



FIG. 1.

APPARATUS FOR DETERMINING MOLECULAR WEIGHT.

constructing this apparatus the stirring device from an old bomb-calorimeter was used. The apparatus, which proved itself to be very handy, is shown in Fig. 1.

In Table I two time–temperature curves are given—a very good and an ordinary one. They show what can be achieved by applying automatically shaking. The results are certainly reliable within 2 per cent.

TABLE I.

| Time, seconds. | Temperature (on Beckmann thermometer). | |
|---|---|---|
| 0 | 3·10 | 3·07 |
| 20 | 2·55 | 2·55 |
| 40 | 2·10 | 2·13 |
| 60 | 2·00 | 2·09 |
| 90 | 2·28 | 2·35 |
| 120 | 2·28 | 2·35 |
| 150 | 2·27 | 2·34 |
| 180 | 2·26 | 2·33 |
| 210 | 2·25 | 2·32 |
| 240 | 2·24 | 2·315 |
| 270 | 2·23 | 2·30 |
| 300 | 2·22 | 2·295 |
| 330 | 2·21 | 2·28 |
| 360 | 2·20 | 2·275 |
| 390 | 2·19 | 2·265 |
| 420 | 2·18 | 2·255 |

*Refractive Index and Specific Refraction.* The refractive index was determined at 20° C. with an Abbe refractor. An accuracy of 0·0002 was attained. The specific refraction was calculated by

$$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}\text{ (Lorentz–Lorenz).}$$

*Dispersion and Specific Dispersion.* With the Abbe refractometer also $n_F - n_C$ was determined at 20° C. According to $n_{G'} - n_C = 1{\cdot}565(n_F - n_C)$ (Cauchy) the dispersion was calculated as $(n_{G'} - n_C) \cdot 10^4$. The specific dispersion is then given as $\frac{n_{G'} - n_C}{d} \cdot 10^4$.

The measurement of dispersion is not as accurate as that of refraction; therefore in the specific dispersion a variation of 5 units is quite possible.

*Aniline Point.* This was determined as prescribed in the I.P.T.–Standard F.O.23. The oils were thoroughly dried with heated calcium chloride before analysing, and then filtered through a dried filter.

*Surface Tension, Parachor and Specific Parachor.* The surface tension was measured by Jaeger's method modified by Nellensteyn.* A platinum capillary was placed vertically in the oil. The capillary was attached to an air-space, and the pressure gradually increased so that the bubble at the end of the capillary increased in size and finally detached itself from the end of it.

The excess pressure above the atmosphere is then equal to the hydrostatic pressure due to the depth of immersion of the capillary in the oil

* See F. J. Nellensteyn and N. M. Roodenburg, "Die Oberflächenspannung-Temperatur Kurven der Asphaltbitumina und verwandter Produkte," *Kolloidchemische Beihefte*, 1930, **31**, 434.

(0·1 mm.) plus the pressure due to the curvature of the drop. The constant of the apparatus was determined by gauging with pure benzol (Kahlbaum) = 28·88 dyne/cm. by 20° C.

The excess pressure is not determined by manometer, reading as indicated by Jaeger, but, according to Nellensteyn, weighted by a balance. By this means the inconvenient manipulation with kathetometers and the application of temperature corrections are eliminated.

As in literature * differences of opinion exist concerning the value of determinations carried out with a capillary with the end plane-ground and a capillary with sharp-ground end, two determinations were carried out in each case :—

1. With a capillary of 1 mm. internal diameter, plane-ground at the end, and,
2. With a 0·6 mm. capillary with sharp-ground end.

The results obtained in these two ways agreed within 0·02 dyne/cm.—that is to say, within the error of measurement which amounted to $\pm$ 0·05 dyne/cm. All determinations were carried out by 20° C. From the figures obtained for molecular weight, density and surface-tension the parachor as $\gamma^{\frac{1}{4}} \frac{M}{D-d}$ was calculated; $\gamma$ being the surface tension, $D$ the density of the oil and $M$ the molecular weight. $d$, being the density of the vapour phase (which is very low at 20° C.), was neglected in the calculation.

The specific parachor was calculated as $\gamma^{\frac{1}{4}} \frac{1}{D}$.

*Diesel Index.* The diesel index needs no further explanation. It was calculated according to the well-known formula :

$$\frac{\text{Aniline-point in °F} \times \text{A.P.I. gravity}}{100}$$

*Elementary Composition.* Carbon and hydrogen were determined by Dennstedt's method, as also by Pregl's microchemical method, the last determination being carried out by Mr. P. J. Hubers, of Amsterdam University.

The agreement of the figures, found by both methods, was very satisfactory. As Mr. Hubers is a specialist in determining the elementary composition of organic substances and as his check-determinations on the oils 1 to 11, agreed for hydrogen in the order of sequence 0·02/0·05/0·03/0·05/0·01/0·08/0·07/0·07/0·09/0·09/0·00, the figures determined by him were preserved as being accurate and given in the table. The maximum divergence for carbon was 0·16 per cent. in duplicate tests.

Sulphur was determined according to the bomb-method A.S.T.M. D129–34.

*Calorific Value (Gross).* As indicated by I.P.T. serial designation G.O.6, special precautions were taken to work as accurately as possible.

* See E. Martin, "Ueber eine absolute Bestimmung der Kapillaritätskonstante mit dem Jägerschen Apparate," *Sitzungsberichten der Kaiserl. Akad. der Wissenschaften in Wien.*, Bd. CXXIII, Abt. 2a, December, 1914.

Thus the room in which the determination was carried out was maintained at constant temperature, and moreover the whole calorimeter was placed in a cupboard with glass screen. Therefore we can certainly guarantee the figures given within $\pm 10$ cal.

*Acidity.* D.I.N. D.V.M. 3658. Expressed as mgm. KOH/gm.

*Bromine Number.* McIlhiney's method. Standard methods I.P.T. 1935, p. 217.

*Flash and Fire Points.* Closed cup Pensky–Martens A.S.T.M. D93–36. Open cup I.P.T.L.O. 7a.

*Conradson Value.* A.S.T.M. D189–36.

*Cloud and Pour Points.* For the original oils the A.S.T.M. D97–34 test was used. As the quantity of oil after hydrogenation was not sufficient for carrying out this test, the oil was then placed in test-tubes and cooled in $CO^2$ acetone, to $-35°$ C. The temperature of the bath was then raised gradually, and from time to time the tubes were observed in order to judge if flow took place or cloud disappeared. A temperature 3° C. above the highest temperature at which the contents of the tube did not flow, was recorded as the pour point.

*Viscosity.* The viscosity was determined by a Vogel–Ossag capillary viscometer. A capillary, with constant 0·0158, was used for the determination. The accuracy of this method was taken as 2 per cent., in all cases duplicate determinations agreeing more closely were obtained. As the kinematic viscosity was determined with the Vogel–Ossag viscometer, the absolute viscosity was calculated by $Vk.\ d = \eta$.

Furthermore, the effect of temperature on viscosity was considered of importance. According to Ubbelohde ("Zur Viskosimetrie," Berlin, 1935) log.log. $(Vk + 0{\cdot}8)$ plotted as a function of log $T_{abs.}$ gives a linear relation. This was verified many times, for low, medium and high viscosity oils for all the determinations of viscosity–temperature curves in our laboratory are checked by the temperature–viscosity chart of Ubbelohde. Therefore this expression can be confirmed, provided no disperse phase is present. Therefore we took the temperature–viscosity relationship of our oils as the tangent of the straight line mentioned, that is :—

$$\frac{\text{log. log. } (Vk + 0{\cdot}8)_{t20} - \text{log. log. } (Vk + 0{\cdot}8)_{t50}}{\log 323 - \log 293}$$

*Distillation and "Kennziffer."* The distillation was carried out by the A.S.T.M. method D158–28.

The "Kennziffer" is given by

$$\frac{t5\% + t15\% + t25\%, \text{ etc., } t95\%}{10}$$

*Cetene Value.* The cetene value was determined by a single-cylinder "National" diesel engine that was converted in our laboratory into an apparatus with which satisfactory results were obtained. As we described this installation in "Fuel in Science and Practice,"* we refer to this publication.

* P. M. van Bemmel and D. J. W. Kreulen. A 5-h.p. "National" diesel engine converted into an apparatus for determining the cetene-value of diesel oils. *Fuel*, 1936, **15**, 336.

*Ring Analysis.* The percentage aromatic rings, naphthenic rings and paraffinic side-chains was calculated from molecular weight, refractive index, density and aniline-point before and after complete hydrogenation as proposed by Vlugter, Waterman and van Westen.*

The great advantage of this method is that the analysis is effected without any chemical or physical separation between groups of hydrocarbons. It possesses this advantage above all other methods; for example, the sulphuric acid method, whereby in removing a single aromatic ring all the attached paraffinic side-chains are also removed.

Therefore the utility of the method mentioned above cannot be over-emphasized.

It is also suggested that further work in this direction should be carried out not only on the chemical composition of lubricating oils (Vlugter) and (in this paper) on gas oils, but that in future the chemical composition also of the other distillation fractions should be investigated.

It is, of course, admitted that this method too has not reached complete perfection; thus it is desirable that apart from the total percentage of paraffins the individual percentage of *n*- and *iso*-paraffins should be determined.

Moreover, in the completely hydrogenated oil the percentage of naphthene rings and paraffinic side-chains is calculated by assuming that 100 per cent. ring naphthenes are present as well as 100 per cent. paraffins, while in reality the side-chains are attached to the naphthene rings. But the number of side-chains present is unknown, and as each augmentation of a side-chain diminishes the number of hydrogen atoms of the naphthenic rings by one, a degree of uncertainty exists in the results obtained. Therefore it would be better to calculate the composition of the oil as the percentage of carbon atoms present in the form of aromatic rings, naphthenic rings and paraffinic side-chains. However, in this publication the method of expression used by Vlugter, Waterman and van Westen is adopted.

The author wishes to express here his sincere thanks to Prof. Dr. Ir. H. I. Waterman and Ir. J. J. Leendertse for the information furnished while carrying out the hydrogenation test. He also wishes to acknowledge the assistance of Mr. J. C. Heynraets in the analysis mentioned in this paper.

*Results.* The results which were obtained are compiled in the Tables II to VII.

## Discussion of Results.

Comparing the figures before and after complete hydrogenation, it is found that, according to the conversion of aromatics into naphthenes, lower figures are obtained for density, refractive index, specific refraction, dispersion, specific dispersion, surface tension and $tg.\alpha$ (that is, the temperature–viscosity relationship of the oil); also the absolute viscosity has a decided tendency to fall. The mean molecular weight, aniline-point, parachor, specific parachor, diesel index, hydrogen and calorific value are higher. Pour and cloud points were found to be approximately the same.

With regard to the Conradson value after hydrogenation, only one test was carried out for the Conradson value in the other cases was so low before hydrogenation that no reliable results could be expected. The single

* *I.P.T. Journal*, 1935, **21**, 661.

TABLE II.

*Density, Mean Molecular Weight, Refractive Index, Dispersion, Aniline Point and Surface Tension before and after Hydrogenation.*

| Oil. | Density, 20/4. | Mean Mol. Weight. | $N_D^{20}$. | $(N_\sigma - N_C)\,10^4$. | Aniline Point, ° C. | Surface Tension, dyne/cm. |
|---|---|---|---|---|---|---|
| | | | *Before Hydrogenation.* | | | |
| 1 | 0·9310 | 180 | 1·5377 | 283 | 7·0 | 31·83 |
| 2 | 0·8889 | 215 | 1·4881 | 164 | 55·1 | 30·47 |
| 3 | 0·9136 | 244 | 1·5034 | 195 | 54·2 | 30·77 |
| 4 | 0·8473 | 192 | 1·4695 | 157 | 56·6 | 28·07 |
| 6 | 0·8605 | 227 | 1·4776 | 161 | 68·9 | 29·17 |
| 5 | 0·8522 | 216 | 1·4741 | 160 | 65·8 | 28·59 |
| 11 | 0·8709 | 251 | 1·4894 | 185 | 72·9 | 30·14 |
| 7 | 0·8511 | 217 | 1·4722 | 158 | 70·6 | 29·00 |
| 8 | 0·8496 | 236 | 1·4758 | 173 | 71·6 | 29·17 |
| 9 | 0·8168 | 198 | 1·4562 | 147 | 72·3 | 27·29 |
| 10 | 0·8387 | 233 | 1·4781 | 159 | 76·0 | 28·88 |
| | | | *After Hydrogenation.* | | | |
| 1 | 0·8528 | 184 | 1·4641 | 128 | 63·4 | 29·16 |
| 2 | 0·8719 | 218 | 1·4725 | 133 | 73·2 | 29·73 |
| 3 | 0·8896 | 261 | 1·4814 | 137 | 80·9 | 30·67 |
| 4 | 0·8279 | 200 | 1·4539 | 127 | 74·2 | 27·69 |
| 6 | 0·8462 | 240 | 1·4624 | 129 | 82·2 | 28·97 |
| 5 | 0·8309 | 226 | 1·4565 | 127 | 82·3 | 28·37 |
| 11 | 0·8433 | 261 | 1·4629 | 131 | 91·3 | 29·56 |
| 7 | 0·8380 | 234 | 1·4591 | 127 | 83·0 | 28·62 |
| 8 | 0·8186 | 235 | 1·4517 | 127 | 90·4 | 28·45 |
| 9 | 0·8051 | 207 | 1·4450 | 123 | 82·3 | 27·26 |
| 10 | 0·8187 | 228 | 1·4518 | 128 | 89·2 | 28·28 |

TABLE III.

*Specific Refraction, Specific Dispersion, Parachor, Specific Parachor and Diesel Index before and after Hydrogenation.*

| Oil. | Spec. Refraction. | Spec. Dispersion. | Parachor. | Spec. Parachor. | Diesel Index. |
|---|---|---|---|---|---|
| | | *Before Hydrogenation.* | | | |
| 1 | 0·3358 | 304 | 459 | 2·551 | 9 |
| 2 | 0·3242 | 184 | 568 | 2·643 | 35 |
| 3 | 0·3238 | 213 | 629 | 2·578 | 29·5 |
| 4 | 0·3290 | 185 | 522 | 2·717 | 46 |
| 6 | 0·3287 | 187 | 613 | 2·701 | 50 |
| 5 | 0·3298 | 188 | 586 | 2·713 | 51 |
| 11 | 0·3316 | 212 | 675 | 2·690 | 49 |
| 7 | 0·3291 | 186 | 592 | 2·727 | 54 |
| 8 | 0·3319 | 204 | 645 | 2·735 | 55 |
| 9 | 0·3329 | 180 | 554 | 2·798 | 66 |
| 10 | 0·3315 | 190 | 644 | 2·764 | 62 |
| | | *After Hydrogenation.* | | | |
| 1 | 0·3236 | 150 | 501 | 2·725 | 49 |
| 2 | 0·3214 | 153 | 584 | 2·678 | 49 |
| 3 | 0·3201 | 154 | 690 | 2·645 | 48 |
| 4 | 0·3270 | 153 | 556 | 2·780 | 64 |
| 6 | 0·3251 | 153 | 658 | 2·742 | 63 |
| 5 | 0·3275 | 153 | 628 | 2·778 | 68 |
| 11 | 0·3266 | 155 | 722 | 2·765 | 70 |
| 7 | 0·3263 | 151 | 646 | 2·760 | 66 |
| 8 | 0·3294 | 155 | 663 | 2·821 | 79 |
| 9 | 0·3306 | 153 | 587 | 2·838 | 78 |
| 10 | 0·3294 | 156 | 642 | 2·817 | 78 |

TABLE IV.

*Elementary Composition, Calorific Value, Acidity and Bromine Value before and after Hydrogenation.*

| Oil. | Elementary Composition. | | | | Calorific Value. | Acidity. | Bromine Value. |
|---|---|---|---|---|---|---|---|
| | H. | C. | S. | Rest. | | | |
| | | | *Before Hydrogenation.* | | | | |
| 1 | 9·73 | 89·39 | 0·21 | 0·67 | 10,240 | 0·10 | 1 |
| 2 | 12·50 | 86·86 | 0·23 | 0·41 | 10,755 | 0·23 | 0 |
| 3 | 12·01 | 87·47 | 0·26 | 0·26 | 10,650 | 0·63 | 0 |
| 4 | 12·94 | 86·20 | 0·51 | 0·35 | 10,825 | 1·55 | 0 |
| 6 | 12·86 | 86·92 | 0·16 | 0·06 | 10,810 | 0·39 | 0 |
| 5 | 12·92 | 86·34 | 0·58 | 0·16 | 10,810 | 0·77 | 2 |
| 11 | 12·51 | 86·95 | 0·43 | 0·11 | 10,725 | 0·06 | 2 |
| 7 | 13·04 | 86·63 | 0·25 | 0·08 | 10,815 | 0·26 | 0 |
| 8 | 12·85 | 85·72 | 1·26 | 0·17 | 10,790 | 0·20 | 0 |
| 9 | 13·57 | 85·65 | 0·26 | 0·52 | 10,955 | 0·12 | 0 |
| 10 | 13·31 | 85·71 | 0·69 | 0·29 | 10,900 | 0·10 | 0 |
| | | | *After Hydrogenation.* | | | | |
| 1 | 13·72 | — | 0·12 | — | 10,940 | — | — |
| 2 | 13·47 | — | 0·14 | — | 10,920 | — | — |
| 3 | 13·33 | — | 0·13 | — | 10,890 | — | — |
| 4 | 14·11 | — | 0·15 | — | 11,025 | — | — |
| 6 | 13·89 | — | 0·13 | — | 10,990 | — | — |
| 5 | 14·16 | — | 0·14 | — | 11,075 | — | — |
| 11 | 14·06 | — | 0·12 | — | 11,035 | — | — |
| 7 | 14·02 | — | 0·15 | — | 11,015 | — | — |
| 8 | 14·37 | — | 0·17 | — | 11,105 | — | — |
| 9 | 14·51 | — | 0·16 | — | 11,125 | — | — |
| 10 | 14·37 | — | 0·15 | — | 11,110 | — | — |

TABLE V.

*Flash and Fire Points, Conradson Value, Cloud and Pour Points, before and after Hydrogenation.*

| Oil. | Flash Points. | | Fire Points. | Conradson Value. | Cloud Points. | Pour Points. |
|---|---|---|---|---|---|---|
| | Closed. | Open. | | | | |
| | | | *Before Hydrogenation.* | | | |
| 1 | 89 | 110 | 115 | 0·04 | $<-35$ | $<-35$ |
| 2 | 93 | 123 | 123 | 0·01 | $<-35$ | $<-35$ |
| 3 | 75 | 101 | 104 | 0·49 | $<-35$ | $<-35$ |
| 4 | 68·5 | 90·5 | 93 | traces | $<-35$ | $<-35$ |
| 6 | 77 | 96 | 112 | traces | not visible | $-34$ |
| 5 | 81 | 109 | 109 | 0·03 | $-13$ | $-31$ |
| 11 | 77 | 101 | 119 | 0·04 | $+14$ | $+8$ |
| 7 | 75 | 97½ | 109 | traces | $-6$ | $-16$ |
| 8 | 87 | 113 | 118 | traces | $+6$ | $-1$ |
| 9 | 81 | 93 | 106 | traces | $-20$ | $-31$ |
| 10 | 97 | 119 | 127 | 0·01 | $-5$ | $-10$ |
| | | | *After Hydrogenation.* | | | |
| 1 | — | — | — | — | $<-35$ | $<-35$ |
| 2 | — | — | — | — | $<-35$ | $<-35$ |
| 3 | — | — | — | traces | $<-35$ | $<-35$ |
| 4 | — | — | — | — | $<-35$ | $<-35$ |
| 6 | — | — | — | — | $<-35$ | $<-35$ |
| 5 | — | — | — | — | $-19$ | $-31$ |
| 11 | — | — | — | — | $+11$ | $+8$ |
| 7 | — | — | — | — | $-6$ | $-16$ |
| 8 | — | — | — | — | $+6$ | $-1$ |
| 9 | — | — | — | — | $-22$ | $-31$ |
| 10 | — | — | — | — | $-3$ | $-10$ |

TABLE VI.

*Viscosity and Distillation before and after Hydrogenation.*

| Oil. | Kinematic Viscosity c.st. | | | Abs. Visc. 20° c.p. | *tg* α. | Distillation. | | | | Kenn–Ziffer. |
|---|---|---|---|---|---|---|---|---|---|---|
| | 20° C. | 38° C. | 50° C. | | | I.B.P. | 25%. | 50%. | 75%. | |
| | | | | | *Before Hydrogenation.* | | | | | |
| 1 | 3·33 | 2·26 | 1·83 | 3·10 | 3·930 | 207° | 233½° | 245½° | 260½° | 249·3° |
| 2 | 7·36 | 4·38 | 3·32 | 6·54 | 4·041 | 220 | 257 | 271½ | 288 | 273·4 |
| 3 | 20·7 | 10·3 | 7·04 | 18·9 | 4·091 | 182 | 254½ | 291 | — | — |
| 4 | 3·25 | 2·25 | 1·83 | 2·75 | 3·787 | 181 | 220 | 236 | 262 | 243·0 |
| 6 | 6·56 | 4·05 | 3·10 | 5·64 | 3·929 | 184 | 253 | 281½ | 311 | 282·7 |
| 5 | 5·23 | 3·35 | 2·62 | 4·46 | 3·891 | 193 | 242½ | 269 | 298½ | 272·3 |
| 11 | 10·4 | 5·98 | 4·42 | 9·06 | 3·897 | 165 | 287 | 311 | 344½ | — |
| 7 | 5·61 | 3·56 | 2·78 | 4·77 | 3·860 | 179 | 252 | 275 | 298½ | 275·9 |
| 8 | 6·93 | 4·32 | 3·31 | 5·89 | 3·790 | 201 | 262½ | 296 | 330 | — |
| 9 | 3·22 | 2·21 | 1·81 | 2·63 | 3·814 | 196 | 227½ | 238½ | 257½ | 245·0 |
| 10 | 5·90 | 3·74 | 2·91 | 4·95 | 3·818 | 217 | 268½ | 283 | 301½ | 285·9 |
| | | | | | *After Hydrogenation.* | | | | | |
| 1 | 3·24 | 2·27 | 1·86 | 2·76 | 3·649 | — | — | — | — | — |
| 2 | 7·05 | 4·29 | 3·26 | 6·15 | 3·956 | — | — | — | — | — |
| 3 | 18·5 | 9·46 | 6·67 | 16·5 | 3·967 | — | — | — | — | — |
| 4 | 3·35 | 2·32 | 1·89 | 2·77 | 3·728 | — | — | — | — | — |
| 6 | 6·79 | 4·19 | 3·21 | 5·75 | 3·879 | — | — | — | — | — |
| 5 | 5·05 | 3·27 | 2·57 | 4·20 | 3·843 | — | — | — | — | — |
| 11 | 10·2 | 6·12 | 4·51 | 8·60 | 3·714 | — | — | — | — | — |
| 7 | 6·15 | 3·91 | 3·01 | 5·15 | 3·808 | — | — | — | — | — |
| 8 | 6·10 | 3·85 | 3·06 | 4·99 | 3·670 | — | — | — | — | — |
| 9 | 3·29 | 2·29 | 1·87 | 2·65 | 3·700 | — | — | — | — | — |
| 10 | 5·67 | 3·65 | 2·86 | 4·64 | 3·735 | — | — | — | — | — |

TABLE VII.

*Cetene Value of Original Oil and Percentage Aromatic Rings, Naphthenic Rings and Paraffinic Side-chains before and after Hydrogenation.*

| Oil. | Centene Value. | Before Hydrogenation. | | | After Hydrogenation. | |
|---|---|---|---|---|---|---|
| | | Aromatic Rings, per cent. | Naphthenic Rings, per cent. | Paraffinic Side-chains, per cent. | Naphthenic Rings, per cent. | Paraffinic Side-chains, per cent. |
| 1 | 23½ | 51 | 8 | 41 | 58 | 42 |
| 2 | 35 | 12 | 49 | 39 | 62 | 38 |
| 3 | 37 | 17 | 44 | 39 | 60 | 40 |
| 4 | 41 | 15 | 27 | 58 | 41 | 59 |
| 6 | 51 | 13 | 30 | 57 | 43 | 57 |
| 5 | 51½ | 16 | 19 | 65 | 35 | 65 |
| 11 | 53 | 20 | 15 | 65 | 34 | 66 |
| 7 | 60 | 12 | 27 | 61 | 39 | 61 |
| 8 | 62 | 19 | 7 | 74 | 26 | 74 |
| 9 | 62 | 12 | 13 | 75 | 25 | 75 |
| 10 | 65 | 13 | 14 | 73 | 27 | 73 |

test carried out, however, makes it quite probable that the Conradson value has a tendency to fall (from 0·49 before to only traces after hydrogenation).

With regard to the sulphur present, this is partly removed during hydrogenation. Oil 8 possessed a strong smell of $H_2S$ after opening the hydro-

genation bomb, indicating that sulphur compounds were probably partly destroyed. This explains why there was no rise in molecular weight after hydrogenation.

It is remarkable that the sulphur is not removed completely; it tends to remain with a certain end-value from 0·12 to 0·17 per cent.

Also the specific dispersion reaches a limiting value. This is in accordance with the observation of Vlugter, Waterman and van Westen, who mentioned that a lubricating oil is practically aromatic-free if the specific dispersion falls below 158. For gas oils this value may be more suitably placed as being below 155 (down to 150). The possibility of obtaining the aromatic content of an oil from the specific dispersion was tested, but no more than a rough approximation could be obtained in that way. It is true that a variation in specific dispersion usually indicates a variation in content of aromatics, and that in some cases a definite relationship is obtained. In other cases, however, a very poor agreement was found. Thus the real aromatic contents of the oils tested were found to be: 51/12/17/15/13/16/20/12/19/12 and 13 and by multiplying the amount of specific dispersion above 153 (mean end-value) by the factor 0·38 (mean factor), we obtain 57/12/23/12/13/13/22/13/19/10 and 14.

As Vlugter, Waterman and van Westen pointed out, for lubricating oils the content of aromatics can be calculated from the rise of aniline-point before and after hydrogenation by multiplying by the factor 0·85. This, however, does not hold good for the gas oils tested. Not only is the factor much higher in our case (as an average : 0·93), but the agreement obtained in this way is not uniform. Thus by multiplication of the rise of aniline-point by 0·93 the following figures were obtained : 52/17/25/16/13/15/17/12/17/9/12. The agreement is better by the specific-dispersion method.

Continuing with our aromatics we can conclude also that a certain connection exists between the rise in calorific value by hydrogenation and the aromatic content of the oil. Although this relationship also is insufficient to base a calculation on it, we can say that roughly each per cent. of aromatics causes a rise of calorific value of 15 calories (min., 13; max., 17).

By calculating the calorific value after hydrogenation from the hydrogen content as found by the specific refraction of the hydrogenated oil, we achieve success. The figures obtained are given in Table VIII.

TABLE VIII.

| Oil. | Calorific Value as Determined. | Calorific Value as Calculated from $290H + 81(100 - H)$. | Difference. |
|---|---|---|---|
| 1 | 10,940 | 10,965 | +25 |
| 2 | 10,920 | 10,915 | − 5 |
| 3 | 10,890 | 10,885 | − 5 |
| 4 | 11,025 | 11,050 | +25 |
| 6 | 10,990 | 11,000 | +10 |
| 5 | 11,075 | 11,060 | −15 |
| 11 | 11,035 | 11,040 | + 5 |
| 7 | 11,015 | 11,030 | +15 |
| 8 | 11,105 | 11,110 | + 5 |
| 9 | 11,130 | 11,135 | + 5 |
| 10 | 11,110 | 11,100 | −10 |

The maximum difference between determined and calculated figure is thus 0·23 per cent. which illustrates a very satisfactory agreement.

Further inquiry was directed to the existence of a connection between the results obtained by the "ring-analysis" and the cetene value—in other words, can the cetene value of an oil be calculated from the figures for aromatic ring, naphthenic ring and paraffinic side-chain content?

From this investigation the formula:

$$\text{Cetene-value} = -0{\cdot}2A + 0{\cdot}1N + 0{\cdot}85P$$

was derived, which formula gives an approximation to the cetene value.

In Table IX the results calculated by this formula are compared with the cetene values of the oils as determined by the engine.

TABLE IX.

| Oil. | Cetene Value as Determined. | Cetene Value as Calculated. | Difference. |
|---|---|---|---|
| 1 | 23½ | 25 | +1½ |
| 2 | 35 | 36 | +1 |
| 3 | 37 | 34 | −3 |
| 4 | 41 | 49 | +8 |
| 6 | 51 | 49 | −2 |
| 5 | 51½ | 54 | +2½ |
| 11 | 53 | 53 | 0 |
| 7 | 60 | 52 | −8 |
| 8 | 62 | 60 | −2 |
| 9 | 62 | 63 | +1 |
| 10 | 65 | 61 | −4 |

In comparing these results, it should be realized that, by engine-testing, a variation of results within 5 units, in figures obtained at different laboratories, must be allowed. The calculated results are, with the exception of those for two oils (4 and 7), within that limit. The deviation found for oil 4 is explicable, as in that case very probably we are dealing with *iso*-paraffins. As Boerlage and van Dyck* have reported, *iso*paraffins, according to the greater or less ramifications of the chain, behave more or less like aromatics.

Now, various figures indicate the presence of relatively high percentages of paraffins in oil 4; thus, the low density, the low surface tension and the high diesel index. However, cloud- and pour-points are low, and together with the low cetene value this is an indication of *iso*paraffins.

For the deviation of oil 7 we cannot find a satisfactory explanation.

With the exception of oil number 7, this investigation is a direct indication that the cetene value is closely related to the chemical constitution of the oil. But as the cetene value is determined more simply by engine test, this statement is not of direct practical value.

* "Causes of Detonation in Petrol and Diesel Engines," *Inst. Automobile Engineers*, March, 1934. See also Lovell, Campbell and Boyd, *Ind. Eng. Chem.*, Jan.–May, 1931, and October, 1933.

In Fig. 2 the specific parachor, the diesel index-number as well as the cetene value, calculated by the formula $-0{\cdot}2A + 0{\cdot}1N + 0{\cdot}85P$, are indicated as a function of the cetene value determined by the engine.

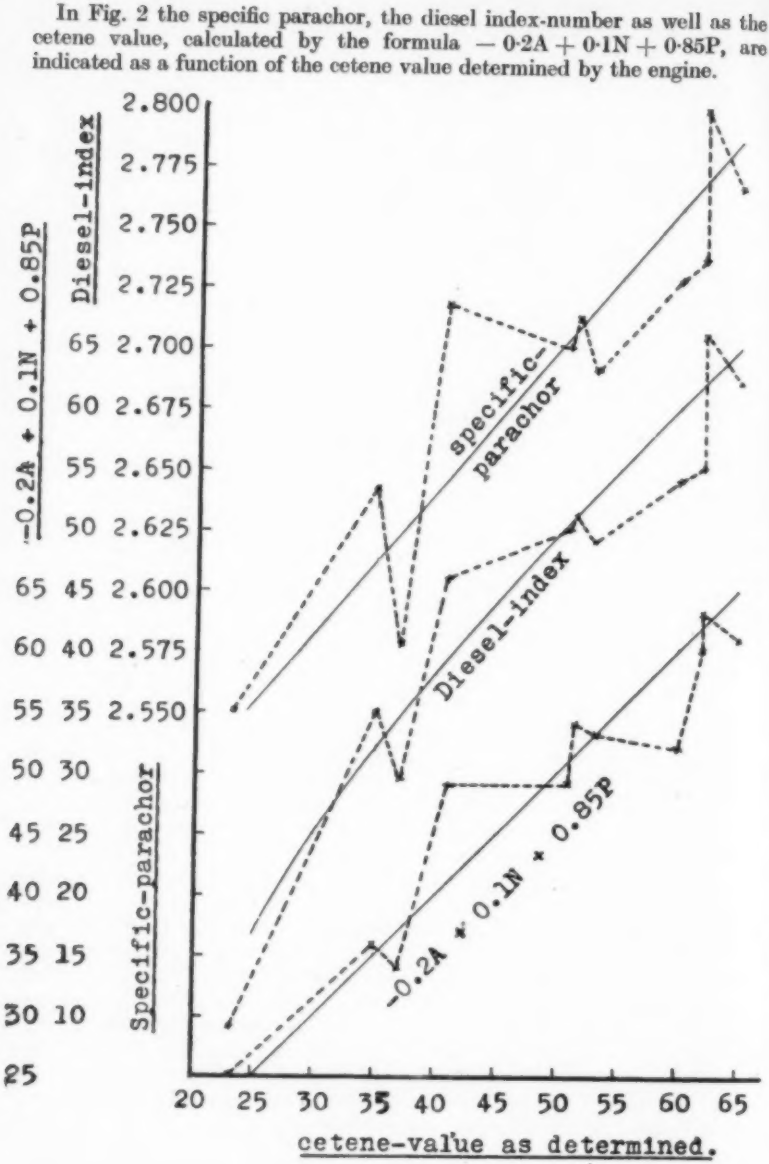



FIG. 2.

RELATIONSHIP BETWEEN SPECIFIC PARACHOR, DIESEL-INDEX AND $-0{\cdot}2A + 0{\cdot}1N + 0{\cdot}85P$ AND CETENE VALUE AS DETERMINED.

The specific parachor is the value to which reference is made in various papers by R. Heinze and M. Marder. It is considered by them as a figure from which the cetene value can be derived with great accuracy. That we cannot confirm; for of the three methods of calculation which are compared, that of the specific parachor is certainly the least accurate. The most accurate, although not fully reliable, are the diesel-index method and the "ring-analysis" method. The diesel-index method has the disadvantage that the cetene value must be calculated with a hypothetical assumption which in itself is not reliable. In our investigations, a greater mean deviation with about the same maximum deviation were confirmed. Thus, we found in order of sequence :— $-2/+2/-4/+6/-1/0/-3/-6/-7/+5/-3$.

It is very remarkable that the lines given in Fig. 2 vary in nearly the same order. So it is with most of the relationships which can be derived from the figures obtained. A certain broad relationship can be enunciated but a definite function cannot be established. It seems very probable that other influences, that have not been elucidated in this investigation, are operative.

So much for the paraffin–*iso*paraffin relationship. It is concluded that where conjugation of the components prevails, its extent, having a corresponding effect on the stability of the molecule, must likewise influence the cetene value.

That such influences could not be followed naturally limits the scope of this paper, but it is hoped that the publication of the results obtained will be of service to future investigators in this field.

# A FAILURE OF THE STANDARD METHOD OF ESTIMATING THE BITUMINOUS CONTENT WHEN APPLIED TO A NATURALLY IMPREGNATED LIMESTONE.

By A. A. Ashworth, M.A., A.M.Inst.C.E. (Member).

The writer was recently requested to estimate the bituminous content of a sample of naturally impregnated limestone.

The content had been previously estimated by others by the standard method of cold extraction with carbon bisulphide and a content of 5 per cent. found.

The writer repeated this cold extraction, and obtained results approximately in agreement. The extraction was, however, very slow, and after continuing the extraction for more than two days the solvent still seemed slightly coloured, showing that extraction was not quite complete.

The extracted rock was then examined, and the colour seemed to indicate a further bitumen content, so it was tested by boiling with a small quantity of trichlorethylene. This gave a very strong coloration, showing that extraction with cold carbon bisulphide extracted only a portion of the bitumen. It was noted that with carbon bisulphide the extracted bitumen was of a very low melting point, probably about 40° C.

It was evident from the above that a hot solvent was much more efficient with the rock than a cold, and as carbon bisulphide boils at 46° C., it is evidently not suitable for a hot extraction.

In order to compare the efficiencies of different solvents, a rough comparison was effected by mixing 1 gm. of powdered rock with 35 c.c. of each of the following solvents: benzene, carbon bisulphide and trichlorethylene. After extraction in the cold for 15 minutes and filtering, a colour comparison showed the order of increasing efficiency to be: benzene, carbon bisulphide, trichlorethylene. A similar extraction, but with boiling trichlorethylene, showed that the hot solvent was much more efficient than the cold.

Based on this, a full extraction with boiling trichlorethylene was made under a reflux condenser, with the result that the rock was found to contain 9·5% of bitumen.

The bitumen extracted by the boiling trichlorethylene was of a different character from that extracted by the cold carbon bisulphide, in that it was of a much higher melting point, being still hard at 100° C.

Although it was found impossible to extract this bitumen from the limestone with carbon bisulphide, when once extracted it was easily soluble in cold bisulphide.

It is not easy to formulate a reason for this failure of the cold extraction with bisulphide, but one possible explanation has been suggested which seems to fit the facts. It is that the rock contains some mineral matter which has strongly adsorptive properties. This might hold the higher-molecular-weight bitumens, just as Florida bleaching earth holds colouring matter from heavy oils. It is known that chlorinated solvents are much

more effective in releasing such colouring matter from used Florida earth than are other solvents.

As further support for this theory, it was noted that it was difficult to free the extracted rock from all traces of solvent. Although trichlorethylene boils at 87° C. it was found necessary to heat the rock to 160–180° C. to free it thoroughly from all traces of solvent.

Additional support for the theory might be found in the avidity with which the dried extracted rock absorbed moisture from the air. It was necessary to transfer the dried rock from the oven to a stoppered weighing-bottle, otherwise it rapidly added weight by absorption of moisture from the atmosphere.

The method of estimating the bitumen content by hot extraction with trichlorethylene appears to be as simple as, and takes a shorter time than, the standard method by cold extraction with carbon bisulphide, so it may be useful to describe the method in detail as used by the writer.

A 1500-ml. wide-mouthed flask is fitted with a cork and reflux condenser. The rock is first crushed so as to pass through a 60-mesh screen and 10 gm. of the powdered rock are weighed.

An ordinary extraction thimble, 22 × 80 mm., is lined with a No. 42 Whatman filter paper, 150 mm. diameter. The filter-paper is pleated somewhat like an umbrella cover, and folded round a cylinder rather smaller in diameter than the extraction thimble, so that it can be inserted in the thimble and line it closely. This filter-paper is necessary, as the texture of the extraction thimble is not sufficiently close to prevent mineral matter passing through into the extract.

The thimble is fitted with a small copper wire stirrup to enable it to be hung below the reflux condenser to a copper wire passing down through the condenser.

A plug of cotton wool sufficient to fill the top of the filter-paper above the crushed rock is also provided. The thimble, with fitted filter-paper, stirrup and cotton wool, is placed in a drying oven and dried for about an hour at 120° C. A glass-stoppered weighing-bottle of sufficient size to hold the thimble is also put in the oven at the same time.

When the thimble assembly is dry, it is placed in the weighing-bottle and weighed. The 10 gm. of rock are then inserted into the filter-paper and topped by the plug of cotton wool, which is pressed down so as to fill the filter-paper, but the top of the plug is kept below the top of the filter-paper. If this is done, there is little danger of the crushed mineral matter creeping over the top of the filter-paper during extraction.

The weighing-bottle with thimble assembly and rock is again placed in the drying-oven for an hour, and afterwards weighed. This will allow the loss in weight owing to moisture in the rock to be estimated.

The 1500-ml. flask is set in a water-bath. The thimble and dried rock are suspended below the reflux condenser, and about 150 c.c. of trichlorethylene put in the flask.

Before inserting the cork with the reflux condenser and thimble in the flask, a small white porcelain crucible is suspended by a copper wire cradle within the flask, the suspending wires passing between the cork and the neck of the flask. The crucible is so suspended that when the cork and thimble are inserted in the flask, the crucible will be about ½ inch below the

bottom of the thimble, but above the liquid in the flask. The object of this crucible is to allow the colour of the solvent passing through the thimble to be observed, so as to judge the progress of the extraction. It also serves to show whether any mineral matter has passed through the thimble during extraction, as most of this mineral matter will collect in the bottom of the crucible.

The extraction is then started, and will probably take about four hours. It will be completed when the solvent runs uncoloured into the crucible.

After a short wait, to allow of cooling and draining of the solvent from the thimble, the cork is withdrawn from the flask. The crucible is carefully examined to see whether there are any traces of mineral matter in the bottom. If there is an absence of mineral matter, it may be safely assumed that none has passed through the thimble during extraction.

The thimble assembly with the extracted rock and a weighing-bottle is placed in the drying-oven. The temperature of this should be allowed to rise to about 160° C. After drying for about an hour, the thimble is at once placed in the weighing-bottle and weighed. This will show the loss in weight of the dried rock due to bitumen extracted. After this weighing, it is advisable to wash through the thimble with a little carbon bisulphide, dry in the air, again place in the drying-oven for a short time and again weigh. The final difference in weight between the dried, extracted rock and the dried rock will give the loss due to bitumen.

If there has been no evidence of mineral matter passing through the thimble during extraction, the trichlorethylene and extracted bitumen are decanted into a distillation flask, and the trichlorethylene is distilled off practically to dryness. The bitumen is then dissolved in a little carbon bisulphide and decanted into a small weighed distillation flask, evaporated to dryness, and the final traces of solvent are removed by a vacuum pump at a pressure of less than 1 mm. abs.

The flask and bitumen are then weighed : this will give the weight of the extracted bitumen, which should, of course, agree with the loss in weight of the extracted rock. In general, there will probably be a small disagreement, the loss in weight of the rock being less than the extracted bitumen. This is probably due to the difficulty in getting rid of all traces of the solvent.

If any traces have been found of mineral matter having passed through the extraction thimble, the solvent and extract, before distillation, must be filtered through a dried and weighed No. 42 Whatman filter-paper. This filter-paper is specified to retain the finest solid matter. The filter-paper is washed through with a little carbon bisulphide, air dried and finally dried in the oven and weighed in a weighing-bottle. This will give the weight of mineral matter which may have passed through the thimble during extraction. This must be added to the weight of the dried, extracted rock, in order to give the correct loss in weight of the rock due to bitumen.

However, in " referee " cases it will be advisable to determine the ash content of the extracted bitumen, even if the trichlorethylene extract contains no mineral matter that can be separated by filtration. The ash, if appreciable, should be " carbonated " (with ammonium carbonate) and the resulting weight deducted from the total bitumen. This may be necessary if the extracted bitumen carries calcium soaps in solution,

although it is open to argument whether such soaps may be regarded as a portion of the asphaltic matter.

One further point which may be of interest arose in connection with the procedure in making the extraction on the water-bath. It was noticed that one extraction was proceeding very slowly, and the cause of this was found to be as follows.

There was a considerable amount of moisture from the water-bath condensed on the outside of the vertical condenser, and this ran down and covered the cork by which the condenser was fitted to the extraction flask. Owing to the joint between the condenser and the cork not being quite tight, a drop or two of this water found its way into the extraction thimble. The presence of this water hindered the extraction from proceeding at the usual rate. On stopping this inleakage of water by tying a string round the condenser above the cork, extraction at once proceeded normally, and was complete in a very short time. The writer understands that a condenser has been suggested with an " umbrella " on the lower tube to overcome this difficulty of water condensation.

It seemed to the writer that the failure of a standard method to give an even approximately correct result would be of interest to anyone dealing with similar problems, and this must be his apology for presenting the above paper.

The method of extraction described was worked out in the Oil Technology Laboratory of the Royal School of Mines by the kind permission of the authorities, to whom the writer's sincere thanks are here tendered.

# ROUMANIAN BRANCH.

## ANNUAL DINNER.

THE Tenth Annual Dinner of the Roumanian Branch of the Institution was held at the Piccadilly Restaurant, Ploesti, on Saturday, 12th December, 1936. MR. C. R. YOUNG, Branch Chairman, presided.

The Dinner was well attended by members and guests, among whom were Sir Reginald Hoare, K.C.M.G., the British Minister; Dr. Nubrecht, the Dutch Minister; Mr. Tanţareanu, Director of Mines; Mr. Bujoui, General Manager of "Petroşani"; Mr. Pennescu-Kertsch, President of Chamber of Commerce; and Mr. A. Beeby Thompson (Member of Council).

The toast of "The Institution of Petroleum Technologists" was proposed by Mr. Pennescu-Kertsch, and replied to by Captain J. E. Treacy. Mr. E. C. Masterson proposed the toast of "The Petroleum Industry of Roumania" in the speech given below. Mr. A. Tanţareanu replied to this toast.

MR. E. C. MASTERSON said: Now that we have nearly reached the end of the year, a general review of the present position and of the immediate future may not be out of place. In the first instance I will consider the production situation, which is perhaps of the greatest interest to the industry at this time.

The year 1936 is likely to show an increase of production over 1935 of about 5 per cent.

The country's production reached the high level of about 2600 cars per day during the summer months of this year, but this level has not been maintained, and, in fact, the level of production to-day is probably the lowest for a considerable time. This is a matter of grave concern. The level of production can, in my opinion, now be increased only by the discovery and development of new structures. The present known structures have passed their peaks, and are now on the decline.

The high level of production in the early part of this year was due to the 1935 discovery of Bucşani. A considerable amount of exploration work has been done this year, but unfortunately the results have been very disappointing. Mărgineni, Aricești, Brăzi, Bucov, Chițoran, Diocești and Podeni are among these.

The industry has realized for some time the necessity of increasing the amount of exploration work in this country, and I am glad to say that the State has also realized the position, and has recently awarded exploration perimeters more liberally than in the past. Consequently 1937 will probably see more exploration work done in Roumania than ever before. The majority of this work will be done in the Plains of Prahova and Dâmbovița, on structures discovered by various prospecting methods carried out at very high costs by the oil companies.

Real exploration work in Roumania has always been on a very small scale, companies having gradually felt their way along fairly well-known structures. Due to the small risks taken, failures have been few. The

number of dry holes in Roumania is about 14 per cent., as compared with nearly 25 per cent. in the United States.

I submit that there has not been a correct balance between exploration work and exploitation in Roumania in the past.

The level of production reached in 1936 will be difficult to maintain, and will require great activity in the direction of exploration. Undoubtedly, whilst the work is going on in the plains of the counties above mentioned, drilling tests should also be carried out in more distant areas, such as Oltenia, Moldavia and eventually Transylvania.

I do not regard the immediate future from the point of view of production with too much optimism, because any exploration work started now which might prove the existence of a producing structure will require several months to develop, and no considerable production could be counted upon from such a structure until the autumn of next year. Therefore, my belief is that 1937 will show a decline in production for this country.

For situations at a considerable distance from the present oil centre of Roumania larger areas should be granted to any one explorer, in order that they may be interesting and economical for the company obtaining such exploration rights. I am glad to say that the projected new mining law provides for such perimeters.

Drilling technique has made the usual progress during 1936. Problems which preoccupied the industry during previous years have been further investigated. Improved technique has allowed of a depth of over 3¼ km. being attained at a well drilled in this country.

As stated previously, 1936 should show an increase in production of about 5 per cent., and should be approximately 8½ million tons.

There have been great improvements in production technique in Roumania, the greatest achievement being, I think, the successful pumping of deep paraffinous wells. New fields are now developed more rationally. Bucşani has been the first rationally produced field in this country. It is admitted that more could have been done, and more will certainly be done in the future; but for a beginning there is no doubt that the achievements at Bucşani are highly creditable, as a result of the close co-operation of the mining office and the producing companies. Bearing in mind, however, my earlier remarks, when I stated that it must necessarily take considerable time before any new structures are developed, I think that the immediate attention of technical men of the oil companies should be directed towards finding ways and means of extracting more and more oil from present producing sands.

It has often been stated that enormous quantities of oil are still left in the sands after a field is abandoned. It is claimed that the recovery from sands varies between such wide limits as 15 and 80 per cent., averaging perhaps 30 per cent., and this figure should give the industry a great deal to think about. In my opinion, this aspect of the business has not received the attention it deserves.

Now we turn to the question of *Refining*: During the past few years there has been no big constructional work in Roumania, apart from one complete new refinery. Very few of the old type shell stills have remained in operation, and practically all the plants are to-day of the tube-still type for topping, combined with separate cracking plants for treating the topped

crude. Most refineries in this country have taken considerable steps towards making their plants economical and more efficient. The result is there if there is an increase in prices—and recent indications are that such a contingency may be possible—our refineries will be found in a very favourable position to take advantage of any such improvement. There has been some construction in vacuum distillation equipment of the tube-still type for the production of lubricating oils and asphalt. Roumanian crudes suitable for economical treatment by solvents are not available in sufficient quantities. The local demand for oils so produced is small, and the present cost of solvent treatment, together with the heavy transport charges to seaboard, do not allow Roumania to produce at prices which can compete with the general world market for solvent oils. One can imagine the difficult position of the Roumanian producers of lubrication oils when one bears in mind that refiners on the seaboard of the Gulf Coast produce lubricating oils in great quantities, and pump them from the refinery straight on to the boats, instead of having to pay, as we do, some 10,000 lei/car f.o.b. charges to Constanta. Also their crude contains sometimes as much as 60 per cent. lubricating oils.

The question of polymerization of gases is also being carefully watched by the Roumanian refiners, but this is not likely to develop in this country in the immediate future.

I pass now to the question of *Consumption*, and divide this into the two natural outlets, of home consumption and export.

The internal consumption has been showing a small but steady improvement, but more can be done to absorb a greater percentage of the Roumanian production on the internal market. Roumania's position will always be dependent on the general world conditions as long as such a great percentage of its production has to be exported. The American position is much more under its own control, as nearly 90 per cent. of its production is used in the home market, whereas in Roumania the position is reversed.

As possible sources of increased consumption I would mention the Roumanian railways, which should use more fuel oil. There are in this country, for instance, a great number of locomotives, equipped with oil burners, burning coal. From figures published recently in the *Monitor de Petrol*, it is estimated that, without any new investment in engine-burners, the fuel-oil consumption could be increased by some 20 per cent., resulting in a saving of some 166 million lei per annum to the C.F.R. Again, the number of motor cars in Roumania is far too low. There has been an increase of only 2 to 3 per cent. in this means of locomotion since 1932, so that to-day Roumania has only some 35,000 cars, or roughly one car to 800 inhabitants, as against one car to five inhabitants in the U.S., and one to 22 inhabitants in France. Any improvement in this direction is out of the question so long as the very high taxes are maintained on the import of cars, thus increasing their initial cost, and on the fuel used. Further, roads in general are still of such a nature as to make motoring anything but a pleasure. In this connection I am very pleased to state that a great deal has been done, and all of us who have lived in this country for some considerable time certainly notice a great improvement. Whilst on the subject of roads, I may say I think the advantages of asphalt roads should continually be im-

pressed upon the authorities by the industry. There are few countries with so many beauty spots as Roumania, and there is not the slightest doubt that as soon as roads are available, very many foreign visitors will be attracted to this country, to say nothing of the local traffic. In this connection I would suggest that the " Oficial National de Turism "—the State organization responsible for fostering touring in Roumania—should work out a scheme, as is done in some other countries, for selling cheaper benzine to motorists touring the country.

When I had the honour of addressing you two years ago, I suggested a way of increasing the consumption of kerosine by insisting upon all carts on the road carrying lamps at night, and I am very glad to see that during this summer this step was taken, and is being rigorously enforced. There is no doubt that roads have been made safer for motoring as a result of this action on the part of the State. Civil aviation should also be developed, and this would also increase the country's consumption of products.

The petroleum industry has done its part in investing about 2¼ billion lei in some 1300 distributing centres scattered all round the country.

In the new Mining Law it is proposed to set up a State monopoly for the internal distribution of products. The only reason for this can be that the State is not satisfied with its present income. It could only get an increased income by increasing taxation, and this would certainly reduce consumption. It could only increase consumption by investing further sums of money in the construction of new depots and by granting credits for sales of products. Can the State do this ?

In 1935, with the existing system, the State received over 13¼ billion lei without any trouble, and without giving any credits. All credits are given to-day by the distributing companies, and the granting of such credits, with the natural risks attached thereto, has no doubt contributed towards the increase in consumption.

Now we turn to *Exports* : In 1935 Italy occupied the first place, Germany followed, England and Egypt were next. In 1936 Germany is holding first place. Exports have shown a steady increase in the past few years, but the value of the exported products has remained fairly stationary. America, which exports only about 11 per cent. of its production, can afford to distribute this at low prices, and this comes into competition with some 85 per cent. of Roumania's production. Roumania is faced also with the Iraq production, which has now reached the capacity of its pipe-line—about 4 million tons per annum, three-quarters of which finds its way into France. The Russian figures for six months of this year also show increased pro duction of about 10 per cent. as compared with last year.

In this connection there are two important difficulties. In the first place, the high transport charges to the seaboard. The cost per km./ton of benzine transported in America is only 18 bani/kgr., as compared with 1·15 lei in Roumania. We used to have trains going to the seaboard made up of 35 cars, then of 50 and now of 70 cars each, but freight charges have remained the same or have increased. The railway authorities are requesting oil companies to invest further sums of money in their tank-cars in order to make the running of such long trains safe. It is to be regretted that this step has been taken rather than the better solution suggested so many times in the past—namely, that of constructing a benzine line to

Constanţa. Undoubtedly that is the only solution to the problem, and the sooner it is realized the better.

The other great difficulty in connection with exports has been the continual change in clearing agreements, export regulations and currency fluctuations. It is hoped that the Government will be able to make satisfactory arrangements with the countries which are natural consumers of Roumanian products, arrangements which will ensure the steady flow of products into these countries.

The fluctuating rates of exchange and the fact that large sums of money have been kept blocked for very long periods have resulted in very serious losses to exporters.

I have attempted to give a brief outline of the position of the industry in Roumania to-day. Let us hope that 1937 will be a good year, that structures being tested will prove productive and, finally, that the Government will do all it can to aid the industry in as many directions as possible.

# ANNUAL REPORT OF THE COUNCIL, 1936.

THE Twenty-Third Annual Report of the Council covering the activities of the Institution during 1936 is presented for the information of the members.

## MEMBERSHIP.

The following Table shows the changes in membership which have occurred during the year, and the total membership on December 31st, 1936.

| | Total Dec. 31, 1935. | CHANGES DURING 1936. | | | | | | | Total Dec. 31, 1936. |
|---|---|---|---|---|---|---|---|---|---|
| | | New. | Transferred to. | Resigned. | Deceased. | Removed. | Transferred from | — + | |
| Hon. Mems. . | 21 | 1 | — | 2 | 2 | — | — | − 3 | 18 |
| Members . | 635 | 56 | 9 | 11 | 6 | 7 | — | +41 | 676 |
| Assoc. Mems. . | 494 | 36 | 12 | 19 | 2 | 9 | 9 | + 9 | 503 |
| Students . | 105 | 23 | — | 3 | — | 3 | 12 | + 5 | 110 |
| Associates . | 90 | 13 | 1 | 3 | — | 3 | 1 | + 7 | 97 |
| TOTALS . | 1345 | 129 | 22 | 38 | 10 | 22 | 22 | +59 | 1404 |

In addition to the above, on December 31st, 1936, 4 Members, 8 Associate Members and 2 Associates had been elected, but had not yet ratified their election, and 30 candidates were awaiting election.

The Council have to record with deep regret the deceases of the following members during 1936 :

| | Date elected. | Class of Membership. |
|---|---|---|
| ANDREW, C. A. . . . . | 1914 | A.M. |
| CLARKE, J. C. . . . . | 1920 | Hon.M. |
| LAMB, W. S. . . . . | 1925 | M. |
| MCKEEVER, C. B. . . . . | 1913 | M. |
| PARKER, A. G. . . . . | 1919 | M. |
| PETAVEL, Sir Joseph . . . . . | 1928 | Hon.M. |
| RICHARDS, H. A. . . . . | 1924 | A.M. |
| SCHLUMBERGER, Prof. C. . . . . | 1934 | M. |
| SUTHERLAND, D. A. . . . . | 1913 | M. |
| WALLEN, E. K.. . . . . | 1921 | M. |

Mr. C. B. McKeever and Mr. D. A. Sutherland were Original Members of the Institution.

His Majesty the King has conferred a Knighthood upon Mr. K. B. Harper for distinguished public service to India and Burma.

His Majesty the King has confirmed the appointment of Mr. R. S. Mackilligan, O.B.E., M.C. (Inspector of Mines and Petroleum Technologist), to be a Nominated Official Member of the Legislative Council of Trinidad and Tobago.

## ACCOUNTS.

The audited Accounts for the year ended December 31st, 1936, together with the Balance Sheet on that date, are submitted.

The Council have to report a surplus of Income over Expenditure due to the steadily growing membership of the Institution and the revenue from the Institution's publications.

A further readjustment of investments has been carried out, and the policy of re-investing in stocks having a definite redeemable date has been continued. During the year investments have been made in Luton 3 per cent. Stock, 1958, Smethwick 3 per cent. Stock, 1951–8, and Bristol 3 per cent. Stock, 1958–63.

A further allocation of £150 has been made to the Branch Fund, and grants totalling £120 18*s*. 2*d*. were made during the year to the Branches.

## Benevolent Fund.

The audited Receipts and Payments Account of the Benevolent Fund for the year ended December 31st, 1936, is submitted.

The thanks of the Council are tendered to all who have contributed to the Fund, and in particular to the Branches and Staffs of various laboratories who have sent "group" contributions.

In December 1936 the Fund received a further donation of £200 to the Specific Endowment Fund administered by the Benevolent Fund Committee.

The Committee has been able to deal promptly with all necessitous cases which have arisen during the year.

## Representation on Other Bodies.

The Institution has been represented on the following bodies :—

The American Society for Testing Materials. Dr. A. E. Dunstan and Mr. G. Sell.
The Advisory Board of the Department of Oil Engineering and Refining of the University of Birmingham. The President.
The British National Committee of the World Power Conference. Dr. A. E. Dunstan.
The Mechanization Board of the War Office. Dr. W. R. Ormandy.
The Ramsay Memorial Laboratory Advisory Committee. Mr. J. Kewley.
The Engine and Fuel Committee (joint Committee with the Institution of Automobile Engineers and the Diesel Users' Association). Dr. A. E. Dunstan, Mr. J. Kewley and Dr. F. H. Garner.
International Electrotechnical Commission. Mr. E. A. Evans.
British Standards Institution, Petroleum Industry Committee. Lt.-Col. S. J. M. Auld, O.B.E., M.C., Prof. J. S. S. Brame, C.B.E., Dr. A. E. Dunstan, Mr. B. J. Ellis, Dr. F. H. Garner, Mr. J. Kewley.
The Institution has also been represented on many other Committees and Panels of the British Standards Institution.
Meetings of the Deutsche Gesellschaft für Mineralölforschung. Lt.-Col. S. J. M. Auld.
South Wales Advisory Committee on Technical Education. Mr. W. C. Mitchell.
British Society for International Bibliography. The Secretary.
Second World Petroleum Congress, Organizing Committee. Dr. A. E. Dunstan, Mr. J. Kewley and the Secretary.

## Meetings of the Institution.

Six General Meetings were held during the year, in addition to the Opening Meeting on the occasion of the Inauguration of the Northern Branch of the Institution at Manchester, and the first Overseas Meeting

held in Holland on May 8th–11th, 1936. A list of the Papers presented and their Authors is given below.

| Date. | Subject. | Author. |
|---|---|---|
| Feb. 11th. | Symposium of Papers on "Welding in the Petroleum Industry." | Various. |
| Feb. 28th. | Inauguration of Northern Branch. "The Application of Science to the Petroleum Industry." | Sir John Cadman, G.C.M.G., D.Sc. |
| March 10th. | Annual General Meeting. Presidential Address. | Sir John Cadman, G.C.M.G., D.Sc. |
| April 6th. | Symposium of Papers on "Oil from Coal." | Various. |
| May 8th–11th. | Holland Meeting. | |
| Oct. 8th. | Short Papers by representatives of the A.F.T.P. | A. de Boulard and X. Normand. |
| Nov. 10th. | Symposium of Papers on "Geophysics." | Various. |
| Dec. 8th. | "The Organisation of Research in the Petroleum Industry." | J. Vermeulen, D. A. Shepherd, and W. C. Asbury. |

### *Meeting in Holland.*

On May 8th–11th, 1936, the Institution held its first Overseas Meeting. By invitation of the Royal Dutch Institute of Engineers, very successful meetings were held in The Hague and Amsterdam. Papers on various aspects of "Diesel Fuels and Transport" were presented at meetings in The Hague, and a series of interesting and valuable visits paid to the laboratories and works of various companies in Delft and Amsterdam.

The thanks of the Council are tendered to the Royal Dutch Institute of Engineers, N.V. de Bataafsche Petroleum Maatschappij, the American Petroleum Company, the Netherlands State Railways, Messrs. Werkspoor, Messrs. Kromhout and the Technische Hoogeschool, Delft, for the hospitality provided, and to Mr. Wouter Cool, Prof. H. I. Waterman and Mr. J. H. C. de Brey as members of the Reception Committee.

### *Annual Dinner.*

The Eighteenth Annual Dinner was held at the Connaught Rooms on Friday, October 9th, 1936, and was attended by about 180 members and their guests. The toast of "The Institution" was proposed by Brig.-Gen. Sir Samuel H. Wilson, G.C.M.G., K.C.B., K.B.E., and Sir Alfred Claud Hollis, G.C.M.G., C.B.E. Mr. F. C. Starling (Director, Petroleum Department) responded to the toast of "The Guests."

## Publications.

### *The Journal.*

Vol. XXII of the *Journal* was published in twelve monthly parts, and contained 19 papers read at General Meetings of the Institution in London, 9 papers presented at meetings of the Branches, 33 contributed articles and 1524 Abstracts of technical literature and patents.

The Council are particularly pleased to record the increasing number of papers which are now submitted for publication in the *Journal* after they have been presented at a meeting of one or other of the Branches.

Owing to the extension of the system of presenting two or more papers on related subjects at a meeting of the Institution, it has been possible to devote several issues of the *Journal* to a single topic. Four issues of the *Journal* contained papers exclusively dealing with "Viscosity," "Solvent Refining," "Welding" and "Diesel Fuels" respectively.

Commencing in January 1936 brief notices of the proceedings of the Council and activities of the Branches were included in a special section of the *Journal* "Institution Notes." This section is also utilized to advise members of new members elected and candidates for election in accordance with the altered procedure of election introduced at the Annual General Meeting of March 1936.

### *Review of Petroleum Technology.*

The Council decided to publish the *Annual Reviews of Petroleum Technology* as a publication distinct from the *Journal*. The reviews of progress during 1935 were published in August 1936 under the title "Petroleum Technology, 1935."

The book contained 24 specially contributed authoritative articles on developments in petroleum technology, and was well reviewed in both the British and American technical press.

## 2ND WORLD PETROLEUM CONGRESS.

The Association Française des Techniciens du Pétrole, the organizing body of the 2nd World Petroleum Congress, has actively carried forward the arrangements throughout 1936 for holding the Congress in Paris on June 14th–19th, 1937.

The Council is acting as the National Committee for Great Britain and the British Empire. The task of collecting Papers for presentation at the Congress is delegated to Reporters for each of the various Sections, and the thanks of the Council are tendered to them for their work in this connection.

The Council was represented on the Organizing Committee by Dr. A. E. Dunstan, Mr. J. Kewley and the Secretary of the Institution.

## STANDARDIZATION.

### *Chemical Standardization.*

The Chemical Standardization Committee has during the year made some re-organization of its Sub-Committees and Panels on lines which will facilitate, and at the same time expedite the work of revision of the Institution's Handbook, *Standard Methods for Testing Petroleum and its Products.*

Several new Panels have been formed, particularly in connection with lubricants.

The Technical Committee on Diesel Fuels, as the result of a considerable amount of work, arrived at a Tentative Method of Engine Test for Diesel Fuels, and this was published in draft form in the *Journal* for comment.

*Engineering Standardization.*

The Engineering Standardization Committee has maintained contact and collaboration with the British Standards Institution on all Engineering Specifications affecting the petroleum industry. Full support has been received from the Engineering Departments of the oil companies, and the thanks of the Council are tendered to the numerous representatives of the Institution on the British Standards Institution Committees.

A list of the Committees and the names of the representatives of the Institution are given below :

Welded Mild Steel Drums. P. M. Tucker.
Metal Containers for Inflammable Liquids. P. M. Tucker, R. L. Sargent, J. E. Jenkins, and E. E. Turner.
Steam Jacketed Pans. E. A. Evans.
Rubber Hose. J. Cuthill and F. W. Springett.
Oil Burning Equipment. N. L. Hudson and P. H. Herring.
Lightning Conductors. C. Dalley.
Steam Flanges. E. T. Forestier and W. A. C. Bowles.
Pipe Fittings and Pipe Threads. B. J. Ellis and W. Wade.
Casing Tubing and Drill Pipe. B. J. Ellis and Aljan Brown.
Furnaces, Ovens and Kilns. I. Lubbock and H. N. Swift.

## Library.

During the past year 381 books and periodicals were loaned to members, as compared with 372 in 1935. A large number of inquiries were dealt with by personal visits, by correspondence and by telephone.

The resources of the Science Library have again been largely drawn upon, and members are reminded that books and periodicals available in the Science Library may be obtained on loan by application to the Librarian of the Institution.

## Awards and Scholarships.

The Redwood Medal of the Institution was awarded to Mr. Harry Ricardo, B.A., F.R.S., in recognition of his distinguished services to the science and technology of petroleum.

The Students' Medal was awarded to Mr. C. S. Newey (Birmingham University) for his paper on "The Dynamics of a Producing Reservoir," and the Students' Prize was divided equally between Mr. Newey and Mr. J. H. Dove (Birmingham University). Mr. Dove's paper was entitled "Viscosity–Temperature Relationships of Lubricating Oils."

No award was made during the year of the Students' Prize presented by Mr. T. C. J. Burgess.

The two Institution Scholarships, tenable at the University of Birmingham and the Royal School of Mines, have been awarded to Mr. A. H. Nissan and Mr. E. N. Tiratsoo respectively.

## Research Fund.

The Research Fund Committee has made grants during the year in assistance of the following investigations :—

"Steels for Use at High Temperatures"; to the British Electrical and Allied Industries Research Association.

"Acid Treatment of Core Samples"; Prof. A. W. Nash.

## Officers for Session 1937–38.

Lt.-Col. S. J. M. Auld, O.B.E., M.C., has been unanimously elected President for the Session 1937–38.

Mr. Ashley Carter, Mr. C. Dalley, Dr. F. H. Garner, Prof. A. W. Nash, Mr. J. McConnell Sanders and Dr. F. B. Thole have been elected Vice-Presidents.

## Branches and Students' Section.

The Council is pleased to report that the Branches of the Institution in Burma, Iran, Roumania, South Wales, Trinidad, and the Northern Branch continue in active progress, and are well supported by members of the Institution locally.

The Annual Reports of the Branches are printed at the end of this Report.

The Council is also pleased to report that the members of the Institution resident in the United States have decided to hold a yearly meeting during the period of the National Sessions of the American Petroleum Institute. Meetings of the U.S.A. members of the Institution were held in Tulsa during May 1936, and in Chicago in November 1936.

The London and Birmingham Branches of the Students' Section carried out successful programmes of meetings and visits to works, of which details are given in the Reports printed below.

The Council desire to tender their thanks to the following for services rendered to the Institution: Lord Plender, G.B.E., Honorary Treasurer; Messrs. Ashurst, Morris, Crisp & Co., Honorary Solicitors; Messrs. Price Waterhouse & Co., Auditors; and the Staff of the Institution.

The Auditors retire and, being eligible, offer themselves for re-election.

By Order of the Council,

ARTHUR W. EASTLAKE,

Honorary Secretary.

## BENEVOLENT FUND.

### RECEIPTS AND PAYMENTS ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1936.

| RECEIPTS. | £ s. d. | £ s. d. | PAYMENTS. | £ s. d. | £ s. d. |
|---|---|---|---|---|---|
| **Balance at Bank on Current and Deposit Accounts, 1st January, 1936 :** | | | **Grants in Aid :** | | |
| Benevolent Fund Account | 487 1 9 | | Benevolent Fund | 34 15 0 | |
| Specific Endowment Fund | 170 0 8 | | Specific Endowment Fund | 100 0 0 | |
| | | 657 2 5 | | | 134 15 0 |
| **Receipts during Year :** | | | **Balance at Bank on Current and Deposit Accounts, 31st December, 1936 :** | | |
| Benevolent Fund : | | | Benevolent Fund Account | 573 16 5 | |
| Donations | 75 4 8 | | Specific Endowment Fund | 271 14 4 | |
| Subscriptions | 37 16 9 | | | | 845 10 9 |
| Income Tax Recovered | 2 3 3 | | | | |
| Interest | 6 5 0 | | | | |
| | | 121 9 8 | | | |
| Specific Endowment Fund : | | | | | |
| Donations | 200 0 0 | | | | |
| Income Tax Recovered | 8 8 | | | | |
| Interest | 1 5 0 | | | | |
| | | 201 13 8 | | | |
| | | £980 5 9 | | | £980 5 9 |

We have examined the above Receipts and Payments Account with the books and vouchers of the Fund and find it to be in accordance therewith. We have verified the Balances with Bankers.

3, FREDERICK'S PLACE,
OLD JEWRY, LONDON, E.C. 2.
*3rd February*, 1937.

PRICE, WATERHOUSE & Co.

## REVENUE ACCOUNT FOR THE

| | £ s. d. | £ s. d. |
|---|---|---|
| To **Administration Expenses :—** | | |
| Staff Salaries and Insurance ... ... ... ... | 1611 19 2 | |
| Printing and Stationery ... ... ... ... | 244 4 7 | |
| General Postages ... ... ... ... ... | 214 14 5 | |
| Telephone, Cables and Telegrams ... ... ... | 24 5 11 | |
| | | 2095 4 1 |
| „ **Establishment Charges :—** | | |
| Rent and Rates ... ... ... ... ... | 449 4 8 | |
| Cleaning and Lighting ... ... ... ... ... | 85 7 5 | |
| Repairs and Renewals ... ... ... ... ... | 71 14 10 | |
| | | 606 6 11 |
| „ **Publications :—** | | |
| Journal Printing ... ... ... ... ... | 1443 0 3 | |
| Abstractors' Fees ... ... ... ... ... | 246 5 6 | |
| Postage on Journals ... ... ... ... ... | 197 16 4 | |
| Cost of other Publications ... ... ... ... | 210 14 8 | |
| | | 2097 16 9 |
| „ **Meetings, Hire of Hall, Preprints, Reporting, Etc.** ... ... ... ... ... ... | | 222 16 11 |
| „ **Library Expenditure** ... ... ... ... ... | | 55 10 1 |
| „ **Students' Scholarships and Prizes** ... ... ... | | 85 5 0 |
| „ **Expenses of Students' Section** ... ... ... | | 33 19 3 |
| „ **Sundry Expenses** ... ... ... ... ... | | 158 16 2 |
| „ **Depreciation of Office and Library Furniture and Library Books** ... ... ... ... ... | | 43 8 9 |
| „ **Auditors' Fee** ... ... ... ... ... ... | | 42 0 0 |
| „ **Grant to Branch Fund** ... ... ... ... | | 150 0 0 |
| „ **Balance for the Year Carried to Balance Sheet** ... | | 268 14 4 |
| | | £5859 18 3 |

## RESEARCH FUND Income and Expenditure

| | £ s. d. |
|---|---|
| To **Grants Made During the Year** ... ... ... ... ... | 55 0 0 |
| „ **Balance as at 31st December, 1936** ... ... ... ... | 316 14 5 |
| | £371 14 5 |

YEAR ENDED 31ST DECEMBER, 1936.

| | £ s. d. | £ s. d. |
|---|---|---|
| By **Subscriptions for 1936 Received :—** | | |
| Members... ... ... ... ... ... ... | 1921 2 6 | |
| Associate Members ... ... ... ... ... | 1139 15 0 | |
| Students ... ... ... ... ... ... | 98 14 0 | |
| Associates ... ... ... ... ... ... | 168 0 0 | |
| | 3327 11 6 | |
| Special ... ... ... ... ... ... ... | 20 0 0 | |
| | | 3347 11 6 |
| „ **Subscriptions in Arrears Received During Year** | | 163 4 6 |
| „ **Publications :—** | | |
| Sale of Surplus Copies of Journal ... ... ... | 1313 7 1 | |
| Advertisements in Journal ... ... ... ... | 534 19 6 | |
| Sales of other Publications ... ... ... ... | 314 17 11 | |
| | | 2163 4 6 |
| „ **Interest and Dividends—Gross** ... ... ... | | 185 17 9 |
| | | £5859 18 3 |

ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1936.

| | £ s. d. |
|---|---|
| By **Balance as at 31st December, 1935** ... ... ... ... | 361 12 8 |
| „ **Interest Received During Year** ... ... ... ... ... | 10 1 9 |
| | £371 14 5 |

## INSTITUTION OF PETROLEUM

*(A Company limited by Guarantee and not*

### BALANCE SHEET AS

| | £ s. d. | £ s. d. | £ s. d. |
|---|---|---|---|
| **Capital of the Institution under Bye-Law Section 6, Paragraphs 14 and 15 :—** | | | |
| *Life Membership Fund—* | | | |
| As at 31st December, 1935 ... ... | 624 0 0 | | |
| New Members during year ... ... | 94 10 0 | | |
| | | 718 10 0 | |
| *Entrance Fees—* | | | |
| As at 31st December, 1935 ... ... | 2647 0 0 | | |
| Additions during year ... ... | 179 11 0 | | |
| | | 2826 11 0 | |
| *Profit on Sale of Investments—* | | | |
| As at 31st December, 1935 ... ... | 326 12 4 | | |
| Profit realised during year ... ... | 24 18 7 | | |
| | | 351 10 11 | |
| *Donations—* | | | |
| As at 31st December, 1935 ... ... | | 326 5 0 | |
| | | | 4222 16 11 |
| **Students Prize and Scholarship Fund :—** | | | |
| As at 31st December, 1935 ... ... | | | 25 0 0 |
| **Branch Fund :—** | | | |
| As at 31st December, 1935 ... ... | | 46 2 6 | |
| *Add:* Grant from Revenue ... ... | | 150 0 0 | |
| | | 196 2 6 | |
| *Less:* Grants made to Branches ... ... | | 120 18 2 | |
| | | | 75 4 4 |
| **Research Fund** ... ... ... ... | | | 316 14 5 |
| **Members' Subscriptions Received in Advance** ... ... ... ... ... | | | 421 9 5 |
| **Journal Subscriptions Received in Advance** ... ... ... ... ... | | | 452 9 1 |
| **Sundry Creditors—General Account** ... | | | 295 13 2 |
| **Revenue Account :—** | | | |
| Balance at 31st December, 1935 ... ... | | 1589 1 10 | |
| *Add:* Surplus Funds of Association of Scientific and Technical Institutions received on its liquidation ... ... | | 177 8 3 | |
| Surplus for year as per separate Statement ... ... ... ... ... | | 268 14 4 | |
| | | 2035 4 5 | |
| *Less:* Honorarium to Associate Editor on his retirement ... ... ... | | 150 0 0 | |
| | | | 1885 4 5 |
| | | | £7694 11 9 |

### AUDITOR'S

We report to the Members of THE INSTITUTION OF PETROLEUM TECHNOLOGISTS and have obtained all the information and explanations we have required. We are correct view of the state of the Institution's affairs at 31st December, 1936, accordby the books of the Institution.

3, FREDERICK'S PLACE,
OLD JEWRY, LONDON, E.C. 2.
*3rd February*, 1937.

TECHNOLOGISTS.

*having a Share Capital.)*

AT 31ST DECEMBER, 1936.

| | £ | s. | d. | £ | s. | d. |
|---|---|---|---|---|---|---|
| **Investments :—** | | | | | | |
| *On Account of Capital—* | | | | | | |
| £461 12 0 3% Conversion Stock ... ... ... | 491 | 12 | 6 | | | |
| 664 6 6 London County Council 3% Consolidated Stock ... ... ... ... ... | 481 | 10 | 6 | | | |
| 806 8 3 Manchester Corporation 3% Stock 1958 | 845 | 17 | 7 | | | |
| 867 8 6 Bristol Corporation 2¾% Redeemable Stock 1955/65 ... ... ... ... | 845 | 17 | 7 | | | |
| 150 0 0 Wandsworth District Gas Co. 5% Debenture Stock ... ... ... ... | 154 | 8 | 6 | | | |
| 400 0 0 Metropolitan Water Board "A" Stock 1963 ... ... ... ... ... | 346 | 10 | 7 | | | |
| 125 0 0 Great Western Railway Co. 5% Consolidated Preference Stock ... ... | 105 | 4 | 9 | | | |
| 150 0 0 Luton Coporation 3% Redeemable Stock 1958 ... ... ... ... ... | 151 | 6 | 7 | | | |
| 150 0 0 Smethwick Corporation 3% Redeemable Stock 1951/8 ... ... ... ... | 151 | 4 | 9 | | | |
| 600 0 0 Bristol Corporation 3% Redeemable Stock 1958/63 ... ... ... ... | 597 | 7 | 3 | | | |
| | | | | 4171 | 0 | 7 |
| (Market Value at 31st December, 1936, £4399.) | | | | | | |
| *On Account of Revenue—* | | | | | | |
| £790 8*s.* 3*d.* 3% Conversion Stock ... ... ... | 842 | 8 | 0 | | | |
| *On Account of Research Fund—* | | | | | | |
| £336 5*s.* 10*d.* 3% Conversion Stock ... ... ... | 357 | 14 | 8 | | | |
| | | | | 1200 | 2 | 8 |
| (Market Value at 31st December, 1936, £1166.) | | | | | | |
| **Office and Library Furniture (excluding Presentations) :—** | | | | | | |
| As at 31st December, 1935 ... ... ... ... | 330 | 6 | 8 | | | |
| *Less:* Depreciation ... ... ... ... ... | 33 | 0 | 8 | | | |
| | | | | 297 | 6 | 0 |
| **Library Books (excluding Presentations) :—** | | | | | | |
| As at 31st December, 1935 ... ... ... ... | 41 | 12 | 7 | | | |
| *Less:* Depreciation ... ... ... ... ... | 10 | 8 | 1 | | | |
| | | | | 31 | 4 | 6 |
| **Members Subscriptions in Arrears (not valued).** | | | | | | |
| **Sundry Debtors and Payments in Advance :—** | | | | | | |
| Sundry Debtors, less Reserve for Doubtful Accounts ... | 199 | 4 | 9 | | | |
| Payments in advance ... ... ... ... ... | 56 | 13 | 5 | | | |
| | | | | 255 | 18 | 2 |
| **Cash at Bank and in Hand** ... ... ... ... | | | | 318 | 11 | 6 |
| **Cash on Deposit, General Account :—** | | | | | | |
| Chartered Bank of India, Australia and China ... ... | 500 | 0 | 0 | | | |
| Post Office Savings Bank ... ... ... ... ... | 920 | 8 | 4 | | | |
| | | | | 1420 | 8 | 4 |
| | | | | £7694 | 11 | 9 |

Signed: JOHN CADMAN, President.
C. DALLEY, Chairman, Finance Committee.
S. J. ASTBURY, Secretary.

## REPORT.

that we have examined the above Balance Sheet with the books of the Institution
of opinion that such Balance Sheet is properly drawn up so as to exhibit a true and
ing to the best of our information and the explanations given to us and as shown

PRICE, WATERHOUSE & Co.

# BURMA BRANCH.

## SECOND ANNUAL REPORT, FOR THE YEAR ENDED DECEMBER 31ST, 1936.

MR. G. W. LEPPER resigned from the Chairmanship at the Annual General Meeting owing to his retiring from the East. The Committee wish to place on record its appreciation of Mr. Lepper's services as the first Chairman of the Branch.

The following Committee was constituted for 1936 :—

| | | |
|---|---|---|
| Chairman : | Mr. W. E. V. ABRAHAM | Elected at Annual General Meeting. |
| Deputy Chairman : | Mr. J. A. BUTLIN | |
| Hon. Sec. and Treasurer : | Mr. C. E. KEEP | |
| | Mr. G. A. F. GRINDLE | |
| | Mr. R. C. PARKER | |
| | Mr. J. RANKINE | |
| | Mr. T. J. F. ARMSTRONG | Remaining on the Committee from the previous year. |
| | Mr. J. L. BENARD | |
| | Mr. E. J. BRADSHAW | |
| | Mr. G. COTTON | |

### MEETINGS.

Six Ordinary General Meetings have been held during the year, five at Yenangyaung and one at Chauk. The following papers were read :—

*Fifth Ordinary General Meeting*, March 13th, 1936.
"The Hard Facing of Oil Well Tools," by E. W. Bentley.
*Sixth Ordinary General Meeting*, May 8th, 1936.
"Repressuring," by J. Coates.
*Seventh Ordinary General Meeting*, August 28th, 1936.
"The Geological Aspects of Deep Drilling Problems," by W. E. V. Abraham.
*Eighth Ordinary General Meeting*, September 25th, 1936.
"Rotary Drilling Equipment for Deep Drilling Conditions," by J. A. Butlin.
*Ninth Ordinary General Meeting*, October 30th, 1936.
"The Preparation and Control of Mud Fluid for Pressure Drilling Conditions," by J. T. Evans.
*Tenth Ordinary General Meeting*, November 27th, 1936.
"Drilling of a Deep Pressure Well in India," by G. F. Wilson.

The average attendance of members and visitors at the above Meetings was forty.

### MEMBERSHIP.

At the close of the year there was on the register of the Branch a total membership of 102, this consisting of forty-two subscribers to the Parent Institution and sixty Branch members.

### FINANCIAL POSITION.

The financial position is detailed in the accompanying statements.

The accounts show an excess of income over expenditure on the year's working of Rs. 445/0/9. At the suggestion of the Committee, the Parent

## BURMA BRANCH.

### Income and Expenditure Account for the Year ended December 31st, 1936.

| EXPENDITURE. | Rs. | As. | P. | INCOME. | Rs. | As. | P. |
|---|---|---|---|---|---|---|---|
| Stenographers' Remuneration | 20 | 0 | 0 | Branch Members' Subscriptions | 290 | 0 | 0 |
| Postage | 12 | 13 | 9 | Grants from Parent Institution for year | 318 | 9 | 0 |
| Rental of Chairs for Meetings | 27 | 0 | 0 | | | | |
| Stationery | 22 | 13 | 0 | | | | |
| Fire Insurance (Epidiascope) | 8 | 7 | 0 | | | | |
| Stand, Screen, Cover, etc., for Epidiascope | 72 | 7 | 0 | | | | |
| Surplus carried to Balance Sheet | 445 | 0 | 3 | | | | |
| Rs. | 608 | 9 | 0 | Rs. | 608 | 9 | 0 |

### Balance Sheet as at December 31st, 1936.

| LIABILITIES. | Rs. | As. | P. | Rs. | As. | P. | ASSETS. | Rs. | As. | P. | Rs. | As. | P. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Sundry Creditors :* | | | | | | | Epidiascope at Cost | | | | 545 | 0 | 0 |
| Parent Institution for cost of Epidiascope | 545 | 0 | 0 | | | | *Sundry Debtors :* | | | | | | |
| *Less* Returned towards advance, £12 @ exchange 1/6 | 160 | 0 | 0 | | | | Parent Institution for 4th Quarter 1936. Grant £6 @ exchange 1/6 | | | | 80 | 0 | 0 |
| | | | | 385 | 0 | 0 | Cash on hand | 91 | 8 | 0 | | | |
| *Surplus Account :* | | | | | | | Cash at Bank | 633 | 4 | 9 | | | |
| Balance carried forward | 519 | 12 | 6 | | | | | | | | 724 | 12 | 9 |
| Transfer from Income and Expenditure Account | 445 | 0 | 3 | | | | | | | | | | |
| | | | | 964 | 12 | 9 | | | | | | | |
| Rs. | | | | 1,349 | 12 | 9 | Rs. | | | | 1,349 | 12 | 9 |

C. E. Keep,
*Hon. Secretary-Treasurer.*

We have examined the books and accounts of the Burma Branch and certify that the above Balance Sheet is correct.

W. A. Delahaye, A.C.A.
R. A. R. Mackay, C.A.

*Khodaung,*
*January 6th*, 1937.

Institution withheld payment of two quarterly grants, thereby reducing to the equivalent of Rs. 385 the indebtedness of the Branch on account of the purchase of the Epidiascope. Cash in hand and at Bank together with the 4th Quarterly Grant for 1936 amount to Rs. 804/12/9, against which has to be placed the outstanding liability of Rs. 385 to the Parent Institution, leaving an overall surplus of Rs. 419/12/9.

W. E. V. ABRAHAM,
*Chairman.*

C. E. KEEP,
*Hon. Secretary-Treasurer.*

*January 8th*, 1937.

## TRINIDAD BRANCH.

### REPORT BY THE COMMITTEE ON THE WORKING OF THE BRANCH DURING THE YEAR ENDED OCTOBER 31ST, 1936.

AT a Committee meeting on November 27th, 1935, Commander H. V. LAVINGTON, R.N., and Mr. H. W. REID were re-elected to serve as Branch Chairman and as Hon. Secretary and Treasurer, respectively.

During the year five meetings were held at which papers were read as follows :—

| | |
|---|---|
| November 27th, 1935. | Eighth Annual General Meeting, followed by a paper by E. C. Scott, Assoc. Member, entitled : "Improved Drilling Speed and its Influence on Cost." |
| January 29th, 1936. | 45th General Meeting. "Costs of Drilling," by H. A. Harris, Associate. |
| February 26th, 1936. | 46th General Meeting. "Present Uses and Future Applications of Cement in Oilfields," by J. L. Harris, Member. |
| March 25th, 1936. | 47th General Meeting. "Some Notes on Gauging and Testing of Crude Oils," by A. H. Richard, Member. |
| April 29th, 1936. | 48th General Meeting. "The Performance of Direct Gas Actuated Plunger Units," by G. A. Walling. |

The average attendance of members and visitors at these meetings was 29.

At the end of the year there were 64 members on the Branch Roll and six candidates were awaiting election.

The sixth Annual Dinner was unavoidably postponed from October 30th to November 7th, 1936. His Excellency the Governor, Sir Murchison Fletcher, honoured the Branch with his presence and proposed the toast of the Institution.

Ninety-eight members and guests were present.

The accounts for the year under review have been audited, and are submitted herewith.

At the request of the Editors of the proposed publication entitled *Science of Petroleum* the Committee undertook to compile an article "The Nature of Crude Petroleum—Trinidad" as a contribution from the Branch. For this purpose Messrs. I. McCullum, H. E. F. Pracy, A. Reid, A. H. Richard and D. M. Walsh were invited to serve as a Sub-Committee with Mr. A. G. V. Berry as Chairman. The Committee wishes to thank the above-

## TRINIDAD BRANCH.

### ACCOUNTS FOR THE YEAR ENDED OCTOBER 31ST, 1936.

#### REVENUE ACCOUNT.

| | $ C | $ C | | $ C |
|---|---|---|---|---|
| To Stenographer's remuneration | | 75 00 | By Quarterly Grants from London | 192 00 |
| „ Printing, Postage, Stationery, Cables, Telephones, etc. | | 35 57 | „ Enrolment Fees | 7 00 |
| „ Cheque Book | | 1 00 | | |
| „ Draft on London, Benevolent Fund | 121 09 | | | |
| *Less* Subscriptions received | 120 40 | | | |
| | | 69 | | |
| „ Surplus for the year | | 86 74 | | |
| | | $199 00 | | $199 00 |

#### BALANCE SHEET AS AT OCTOBER 31ST, 1936.

*Revenue Account :*

| | $ C | | $ C |
|---|---|---|---|
| Surplus brought forward | 121 22 | To Balance at Bank | 368 81 |
| Surplus for the year | 86 74 | „ Cash in Hand | 9 15 |
| Subscriptions received for 6th Annual Dinner—in advance | 170 00 | | |
| | $377 96 | | $377 96 |

H. V. LAVINGTON, *Chairman.*

H. W. REID, *Hon. Secretary and Treasurer.*

F. MIDDLETON, D. M. WALSH } *Auditors.*

mentioned members for the part they took in compiling the article, which was duly forwarded to the Editors in London.

The Committee was also requested to obtain papers from members of the Branch to be read at the Second World Petroleum Congress which is to be held in Paris in 1937. This matter is still receiving attention.

The Committee has great pleasure in recording the thanks of the Branch to Mr. F. Middleton and Mr. D. M. Walsh for serving again as Honorary Auditors, and to the President and Members of the Apex Club for the continued use of their Club House for Meetings.

H. V. LAVINGTON,
*Chairman.*

H. W. REID,
*Hon. Secretary and Treasurer.*

## NORTHERN BRANCH.

### REPORT OF COMMITTEE FOR YEAR ENDED DECEMBER 31ST, 1936.

THE Northern Branch of the Institution of Petroleum Technologists was inaugurated in December 1935, when a local Committee was formed under the guidance of several prominent Members of the Council. Mr. H. C. S. Fothergill was unanimously elected Chairman, and Mr. John E. Bennion, Honorary Secretary, of the Northern Branch.

The opening General Meeting of the Branch was held in Manchester on February 28th, 1936, when, to an audience of about 400 people, the President of the Institution, Sir John Cadman, G.C.M.G., D.Sc., delivered a lecture entitled "The Application of Science to the Petroleum Industry." Sir John Cadman was welcomed to the City at an informal dinner which preceded the Meeting, by the Right Honourable, the Lord Mayor of Manchester and many leading industrialists.

At the commencement of the present session the Branch numbered 179 members, which included 41 members of the Parent Institution.

During the session a very successful series of meetings has been held and visits have been made to the Lobitos Refinery, the Shell-Mex & B.P. Installation at Ellesmere Port, and the Blending and Candle Works of the Anglo-American Oil Company at Trafford Park.

Contact has been made with the Manchester Chemical Societies Joint Advisory Committee, and the Northern Branch of the Institution is now a constituent Society of this body. It has thus been possible to arrange joint meetings with some of the other technical Societies in the district for the consideration of matters of mutual interest. Joint Meetings have been held with the local Section of the Society of Chemical Industry, the Oil and Colour Chemists' Association and the Institute of Fuel. All the meetings have been well attended, the average attendance being about 100 members. Interest in the Branch is sustained and the membership continues to show a steady increase. The present membership is 236, an increase of 57 over that at the commencement of the Session. The Syllabus of Meetings is as follows :—

| | |
|---|---|
| February 28th, 1936. | "The Applications of Science to the Petroleum Industry," by Sir John Cadman, G.C.M.G., D.Sc. |
| March 20th, 1936. | "The Science of Lubrication," by F. J. Slee, B.A., B.Sc. |
| October 21st, 1936. | Joint Meeting with Institute of Fuel. "Diesel Engines and Diesel Oils," by L. J. Le Mesurier, M.I.N.A., M.I.Mar.E., M.I.P.T. |
| November 18th, 1936. | "Interesting Applications of Petroleum," by C. Chilvers, M.A., F.I.C., F.C.S. |
| December 16th, 1936. | Joint Meeting with Institute of Fuel. "High Performance Fuels," by H. C. Tett, B.Sc., A.R.C.S., D.I.C. |

Early in the present Session the Committee considered the inauguration of a scheme of systematic instruction in Petroleum Technology. The Sub-Committee formed to institute inquiries to this end approached the educational authorities of the City, and as a result of this, a five-year Course of part-time technical education in Petroleum Technology was commenced at the College of Technology, Manchester, in October 1936. This Course has been designed along lines similar to those adopted by other Technical Institutions for Courses which lead the students through appropriate certificates, to qualification for admission to the Institution concerned. The Course in Petroleum Technology includes as ancillary subjects, Mathematics, Physics, Mechanics, Chemistry and Applied Thermodynamics. Petroleum Technology is dealt with in Lecture and Laboratory classes concerned with the production and refining of petroleum and the utilization of the products.

The Committee recognized that such a Course as the above, extending over a period of five years, whilst suited to the requirements of the junior personnel of the industry, did not provide for the older members of the Branch who wish to have adequate instruction on the technical developments of the industry.

For salesmen, refinery workers, laboratory assistants and depot and departmental employees a course of Lectures by Mr. E. J. Dunstan on Petroleum Technology, which are generally of an introductory character, has been arranged. These lectures are included at an early stage in the above Course, since they serve also to introduce the systematic student to advanced lectures and laboratory work which come later in his Course. For men engaged at the Ellesmere Port Oil Basin, which is too far removed from Manchester to allow of attendance at the Classes at Manchester College of Technology, it has been arranged that a series of lectures shall be given at Ellesmere Port. The organization of these is due largely to the initiative of Mr. J. S. Parker of the Lobitos Oil Company, Mr. S. J. Newlove of the Anglo-American Oil Co. Ltd., and Mr. H. Makey of Shell-Mex and B.P. Ltd., respectively, who secured the willing co-operation of the Director of Education for Cheshire, Mr. F. F. Potter, and the Deputy-Director, Dr. Kellett.

It is almost certain that evening classes in Petroleum Technology will be available in the autumn of 1937 at Ellesmere Port for students who qualify for the Intermediate Examination of the City and Guilds of London Institute.

The Committee of the Northern Branch considers that, whilst these developments towards providing the Industry locally with a well-trained and informed personnel are promising, it will be possible to take more energetic measures in the near future to implement and widen their scope.

In conclusion, the Committee is pleased to report that the financial position of the Branch is satisfactory.

H. C. S. FOTHERGILL, *Chairman.*

J. E. BENNION, *Hon. Secretary.*

## STUDENTS' SECTION (LONDON BRANCH).

### THIRTEENTH ANNUAL REPORT.

AT December 31st, 1936, the membership of the Branch was as follows :—

| | |
|---|---|
| Student Members . . . | 55 |
| Associated Students . . | 12 |
| | 67 |

THE number of Student Members showed an increase of one over the previous year and the Associated Students were elected under the scheme approved by Council at the end of last year.

The following were elected at the Thirteenth Annual General Meeting held on February 18th, to serve on the Committee for the Session 1936–37 : Messrs. Barrett, Boyd, Bridgwater, Fasola, Ferguson, Groves, Keach and Wright. Messrs. Boyd, Fasola and Groves subsequently tendered their resignations, and Messrs. Kirby and Haworth were elected to fill two of the vacant places. Messrs. Keach, Barrett and Ferguson were elected Chairman, Vice-Chairman and Hon. Secretary respectively.

During the year the following ten meetings and five visits were held :—

| | |
|---|---|
| January 21st, 1936. | Joint Meeting with Graduates Section (London Branch) I.A.E. "Recent Developments in Aero Engine Design," by E. L. Bass. |
| February 4th, 1936. | Second of series of special Geographical lectures. "Trinidad, Venezuela and Central America," by Professor L. Rodwell Jones. |
| February 18th, 1936. | Annual General Meeting. "Migration and Accumulation of Oil," by P. E. Groves (Student). |
| February 26th, 1936. | Visit to London and Thames Haven Oil Wharves, Ltd., Thames Haven. |
| " " " | Annual Dinner. |
| March 11th, 1936. | Visit to Anglo-Iranian Oil Co., Ltd., Research Station, Sunbury. |
| " " " | Meeting at Sunbury. "Solvent Extraction," by J. A. Oriel. |
| March 24th, 1936. | Third of series of special Geographical lectures. "Iran," by James Bayliss. |
| May 5th, 1936. | Visit to Messrs. Firestone Tyre and Rubber Works, Brentford. |
| May 19th, 1936. | "Oilfield Waters," by R. I. Martin (Student). |
| October 6th, 1936. | "Technical Aspects of Lubricating Oil Sales," by W. E. Gooday. |
| October, 21st, 1936. | Visit—Messrs. Lewis Berger's Works. Homerton. |
| November 5th, 1936. | "Asphalt," by A. D. Davidson (Student). |
| November 17th, 1936. | Annual Open Meeting. "Recent Developments in Refinery Technology," by Professor J. S. S. Brame. |
| December 1st, 1936. | Visit to Messrs. Prices Patent Candle Co.'s Works, Battersea. |
| December 15th, 1936. | Joint Meeting with Graduates and Students Sections (London Branches), I.A.E. and R.Ae.S. "Fuels for Aero Engines," by C. H. Barton. |

Although it would appear that the number of Student papers is less than usual, it will be found that taking the whole of the two Sessions 1935–36 and 1936–37, the actual proportion of Student papers is higher.

The meeting on March 11th was held by the courtesy of the Anglo-Iranian Oil Co. at their Research Station at Sunbury after a tour had been made of the Laboratories, etc. This proved a very successful innovation, and meetings and visits are being arranged at other centres.

A meeting of the Chairmen and Secretaries of the Graduates and Students Sections (London Branches) was convened by the Chairman and Hon. Secretary, and was attended by representatives from the following Institutions: Institute of Marine Engineers, Institutions of Electrical, Civil, Chemical, Structural Production and Automobile Engineers and the Royal Aeronautical Society. Subsequently seven of these bodies co-operated with the Branch in the production of a Joint Programme, and an agreement was made whereby members of one Branch could attend the meetings and socials of any other Branch. This Joint Programme was very well received, and will be published in two parts annually. It is confidently expected that the co-operation of these Junior Branches will prove of great mutual benefit.

The attendance at the meetings and visits during the year has been fairly satisfactory, although on one or two occasions it has shown a marked falling off. It is hoped that there will be some improvement during the coming year. The Annual Dinner was once again quite successful, and the Branch had the pleasure of entertaining a number of visitors and guests, including several senior members. The practice of holding Informal Dinners after the meetings has been continued and they have, in general, proved to be quite popular.

No member of the Branch was successful in obtaining any of the Institution's awards. The small number of entries from London is to be deprecated, and it is to be hoped that there will be some improvement during 1937.

The Branch prize for the best contribution to the discussion at meetings throughout the Session 1935–36 was awarded to H. E. W. Kirby. The level of discussion has shown noticeable improvement.

The Committee would like to congratulate E. N. Tiratsoo on being awarded the R.S.M. Scholarship.

At the end of the 1935–36 Session Mr. Bridgwater was forced to resign his office of Chairman, due to pressure of business, and the Committee would like to take this opportunity of expressing its appreciation of the excellent work which Mr. Bridgwater did during his tenure of office. There is no doubt that the increased activity of the Branch has been due largely to his efforts. Thanks are also due once again to Mr. Ashley Carter, who, as Council's representative on the Committee, has always shown so much active interest in the Branch, to other Senior Members who have helped in many ways and to the Secretary and Staff of the Institution for the assistance which they have rendered.

R. H. KEACH,
*Chairman.*

B. C. FERGUSON,
*Hon. Secretary.*

*February 2nd*, 1937.

# STUDENTS' SECTION (BIRMINGHAM BRANCH).

## ANNUAL REPORT.

THE Committee has pleasure in presenting the Fourteenth Annual Report and Statement of Accounts for the year ended December 31st, 1936.

At the Annual General Meeting the following Officers and Committee for this Branch were elected :

A. NISSAN (Chairman).
E. M. HOLBROOK (Vice-Chairman).
L. V. W. CLARK (Hon. Secretary and Treasurer).

Additional members of the Committee :—

V. G. NORRIS.
E. B. SANGSTER.

During the year six meetings were held and the following papers read :—

| | |
|---|---|
| January. | "Burma and the East Indies," by Dr. Dudley Stamp. |
| do. | "The Value of Research to the Oil Industry," by Dr. A. E. Dunstan. |
| February. | "Venezuela and Mexico," by Dr. Rodwell Jones. |
| May. | Annual General Meeting. |
| do. | "Iran," by Mr. Bayliss; paper read by Mr. L. V. W. Clark. |
| November. | "The Progress of the Petroleum Industry in the U.S.A.," by Dr. A. E. Dunstan. |

The attendances during the year showed a slight increase, which it is hoped to maintain during the coming session.

The Committee would like to congratulate Mr. C. S. Newey on being awarded the Students' Medal and on sharing the Students' Prize with Mr. J. H. Dove.

L. V. W. CLARK,
*Hon. Secretary.*

## BIRMINGHAM BRANCH.

### ACCOUNTS, 1935–1936.

| Credit. | £ | s. | d. | Debit. | £ | s. | d. |
|---|---|---|---|---|---|---|---|
| By Balance brought forward . | 8 | 4 | 1 | To Teas . . . . | 4 | 12 | 4 |
| „ Cheque from I.P.T. . . . | 7 | 7 | 0 | „ Expenses for teas . . | | 15 | 0 |
| | | | | „ Sundries . . . | | 4 | 9 |
| | | | | | 5 | 12 | 1 |
| | | | | Balance in hand . . | 9 | 19 | 0 |
| | £15 | 11 | 1 | | £15 | 11 | 1 |

A. NISSAN.
*Chairman.*

L. V. W. CLARK,
*Hon. Secretary and Treasurer.*

## SOUTH WALES BRANCH.

MEMBERSHIP of the Branch has been well maintained and average attendance at meetings still keeps above the fifty mark.

Our really big event was the visit of Sir John Cadman, when, on throwing open the meeting, we had approximately 350 people present to listen to an address built round the film of the Iraq pipe-line.

We had also an extremely interesting paper from Dr. Thole.

Since the turn of the year the only paper exclusive to our members was on "Boiler Feed Water," which was well attended.

We are looking forward to the visit of Prof. Brame in a week's time, and also to a paper of a geological character before the session closes.

We have, through the joint societies, been able to provide our members with attractive lectures by Dr. Pratt upon such subjects as the defence of the civil population against gas—a very topical subject at present—and to those of a chemical turn of mind there have been excellent papers on advances in inorganic chemistry and a practical paper on flocculation.

Whilst these subjects are perhaps rather loosely connected with petroleum matters, these papers, which are open to all the participating scientific societies of South Wales (of which we are now one), do maintain a scientific interest which cannot be other than good for those whose interests might be otherwise confined exclusively to petroleum matters.

E. THORNTON,
*Hon. Secretary.*

*Llandarcy,*
*February 17th*, 1937.

## SOUTH WALES BRANCH.

### Income and Expenditure Account for Year to April 30th, 1936.

| EXPENDITURE. | £ | s. | d. | INCOME. | £ | s. | d. |
|---|---|---|---|---|---|---|---|
| To Expenses of I.P.T. Meeting at Hotel Metropole, 6.12.1935 | 3 | 1 | 0 | By Members' subscriptions (Branch) | 7 | 12 | 6 |
| „ Canteen charges for teas supplied prior to Lectures | 3 | 10 | 4 | „ Balance, being excess of Expenditure over Income, carried to Balance Sheet | 1 | 1 | 10 |
| „ 1–220-volt 500-watt Epidiascope lamp | 1 | 5 | 0 | | | | |
| „ Hire of Lantern Sheet, 7.10.1935 | | 7 | 6 | | | | |
| „ Hotel Metropole expenses *re* Swansea Joint Scientific Societies | | 10 | 6 | | | | |
| | £8 | 14 | 4 | | £8 | 14 | 4 |

### Balance Sheet as at April 30th, 1936.

| | £ | s. | d. | £ | s. | d. | | £ | s. | d. |
|---|---|---|---|---|---|---|---|---|---|---|
| Balance as at May 1st, 1935 | 27 | 9 | 6 | | | | Cash at Bank | 26 | 7 | 8 |
| *Deduct* :— | | | | | | | | | | |
| Balance transferred from Income and Expenditure Account | 1 | 1 | 10 | | | | | | | |
| | | | | 26 | 7 | 8 | | | | |
| | | | | £26 | 7 | 8 | | £26 | 7 | 8 |

W. C. Mitchell,
*Chairman.*

E. Thornton,
*Hon. Secretary and Treasurer.*

## ROUMANIAN BRANCH.

THE Committee have pleasure in presenting the Tenth Annual Report for the year ending December 31st, 1936, together with the accounts to this date.

RECEIPTS AND EXPENDITURE ACCOUNT FOR YEAR ENDED 31ST DECEMBER, 1936.

| | *Lei.* | | *Lei.* |
|---|---|---|---|
| Surplus on Annual Dinners . | 6,501 | Debit Balance at 31/12/35 . | 2,267 |
| | | Postage . . . . . | 2,160 |
| | | Expenses of Meetings . . | 400 |
| | | Printing . . . . . | 462 |
| | | Balance in hand at 31/12/36 . | 1,212 |
| | 6,501 | | 6,501 |

The Branch register shows the following list of Members :—

| | |
|---|---|
| Honorary Members . . . . . | 1 |
| Members . . . . . | 30 |
| Associate Members . . . . . | 15 |
| Students . . . . . | 2 |
| | 48 |

which is the same number as compared with a year ago.

The Committee wish to place on record their deep regret at the death of one of the Members, Mr. E. K. Wallen, and also at the departure of Mr. J. Chaillet, ex-Chairman of the Branch.

The Ninth Annual General Meeting was held on 6th March, 1936, at which the Chairman, Mr. P. R. Clark, retired, and was succeeded by Mr. C. R. Young. The Chairman announced that Messrs. Masterson and Leitch retire from the Committee in rotation. Mr. Leitch did not seek re-election. No new nominations were received, therefore Mr. Masterson was re-elected without opposition.

Two General Meetings were held during the year at which the following papers were read :—

6th March, 1936. *Fifty-third General Meeting.*
"Cracking and Polymerization," by Dr. Suciu.
27th November, 1936. *Fifty-fourth General Meeting.*
Mr. G. Elias led the discussion on "Deep Well Drilling."

The Tenth Annual Dinner was held on 12th December, 1936, under the chairmanship of Mr. C. R. Young, and 66 members and visitors were present.

Members of the Committee were :—

Mr. C. R. YOUNG, *Chairman.*
Mr. E. C. MASTERSON.
Mr. D. I. MAXWELL.

Mr. I. S. RUTHERFORD.
Captain J. E. TREACY, *Honorary Treasurer.*
Mr. O. A. BELL, *Honorary Secretary.*

The ex-officio Members of the Committee were :—

Mr. J. L. CHAILLET.
Mr. ION EDELEANU.
Mr. P. R. CLARK.

The Committee again wish to record their thanks to the Chamber of Commerce, Ploesti, for the use of their Hall for the Meetings during the 1936 Session and to Messrs. Brazier and Suciu for acting as Honorary Auditors.

C. R. YOUNG,
*Chairman.*

O. A. BELL,
*Hon. Secretary.*

# THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

## Annual General Meeting.

The Twenty-fourth Annual General Meeting of the members of the Institution was held at the House of the Royal Society of Arts, John Street, Adelphi, London, W.C.2, on Tuesday, March 9th, 1937, at 5.30 p.m. Mr. Ashley Carter, Vice-President, occupied the Chair.

The Secretary (Mr. S. J. Astbury) read the notice convening the meeting, the report of the Auditors, and the certificate of the Auditors to the Benevolent Fund Account.

The Minutes of the Twenty-third Annual General Meeting, held on March 10th, 1936, were read and signed by the Chairman.

The Chairman announced that the method of election of members of the Council had had to proceed on somewhat different lines than in the past. Six members of Council were due to retire under the provisions of the By-Laws. One of these, Mr. James Romanes, did not desire his name to be put forward for re-election. One new nomination had been received, viz., that for Mr. H. C. Tett. There had, therefore, been no necessity for the ordinary procedure of ballot, as there were six nominations for six vacancies on the Council. He would therefore submit to the meeting that the following six Members be elected members of Council:

E. A. Evans, F.C.S.
W. E. Gooday, A.R.S.M., D.I.C.
A. C. Hartley, F.C.G.I., M.Inst.C.E., M.I.Mech.E.
C. A. P. Southwell, M.C., B.Sc.
A. Beeby Thompson, O.B.E., M.I.Mech.E.
H. C. Tett, B.Sc., D.I.C., A.R.C.S.

This was carried unanimously.

It was agreed that the list of Honorary Members, Members, Associate Members, Students and Associates elected or transferred between January 1st, 1936, and December 31, 1936, be laid on the table.

The Chairman said that in the unavoidable absence of the President, Sir John Cadman, who on account of his absence abroad had asked him to express his regrets at not being able to preside that evening, he now had pleasure in submitting for approval the Twenty-third Annual Report of the Council, together with the Revenue Accounts for the year ending December 31st, 1936, and the Balance Sheet at that date. Copies of these had been circulated to all Members, and with their approval would be taken as read. (*Agreed*).

Although Sir John was not present, it was typical of his keen personal interest in the Institution, that he was taking the opportunity, during his travels, to establish personal contact with some of the overseas members.

Before dealing with the activities of the Institution and its members during the year 1936, he had to express Sir John Cadman's warm appreciation and thanks for the loyal co-operation which the members and staff of the Institution had extended to him during his particularly happy second term of Presidency. It was indeed an honour and privilege to him (Mr. Ashley Carter) to represent the Council on the present occasion; the duty was a most pleasurable one, as during the year 1936 the Institution had continued to progress in every direction—in fact, more so than during any previous year of its existence. The earlier years had been necessarily those of consolidation which, having been effected, placed the Institution now in the position of being able to widen its activities.

The Report submitted first dealt with membership, this showing a total of 1404, which was an increase of over 4 per cent. as compared with the end of 1935. In addition to this total there was a Branch membership of no less than 328. There was thus opened up a considerable potential accession of membership to the Institution. The Branches admitting Branch membership were Burma, the Northern Branch, the South Wales Branch, and the Students' Section (London Branch). The Branch membership indicated a vigorous activity, on which the Council desired to congratulate all those concerned.

He refrained from any comment on the financial position of the Institution, as that would be dealt with by Mr. Dalley, the Chairman of the Finance Committee.

He recommended to members' attention the position of the Benevolent Fund, and without any hesitation solicited donations to that worthy sphere of the Institution's activities. By the past generosity of donors, they were starting to build up the fund, but it should be remembered that there was a growing membership, and the total of the fund per capita was a very small figure. Donations would be most gratefully accepted and faithfully dealt with after sympathetic and careful investigation, by the Committee appointed to administer assistance to those in need. The Committee was always considering ways and means of augmenting the fund, and would gladly welcome constructive suggestions from members. On behalf of the Committee he wished to express their grateful appreciation to all who had so generously contributed.

It would be seen from the Report that the Institution was represented on several scientific bodies. He wished to mention one further representation, viz., Dr. P. E. Spielmann on the Permanent International Association of Road Congresses. This Association met annually in a selected European country.

An important innovation during the year 1936 had been the holding of a meeting in Holland, by the invitation of the Royal Dutch Institute of Engineers. The meeting, which was held in lieu of the summer meeting, had been attended by seventy members, who were most hospitably entertained during the four days' visit. So impressed was the Royal Dutch Institute of Engineers with the success of the meeting, that they had immediately decided to form a Petroleum Section. This Section had a membership of over 100. A cordial invitation had been extended to the Institution to visit the German oilfields in the vicinity of Hanover, but it had been found to be impracticable, on account of the lengthy time involved.

This visit to Holland was one which furnished an opportunity for our secretary, Mr. S. J. Astbury, to render further proof of his organizing abilities, and which, as pointed out above, had such gratifying results.

There was an ever-increasing demand for the *Journal*, which fact in itself showed the well-merited appreciation it was receiving. The Publication Committee, under the untiring energy and outstanding ability of its Chairman, Dr. Dunstan, had produced a set of *Journals* during the year of which the Institution had every right to feel proud. A new feature added during 1936 had been the inclusion of notes of activities of the Institution, by which members were kept *au fait* with developments.

Reference was made in the Report to the forthcoming second World Petroleum Congress to be held in Paris from June 14th to 19th. It was hoped that the full support of members would be given to this Congress, of which full details were about to be issued. Over 250 papers had already been promised, and, in addition, various visits had been arranged. There was every prospect of an instructive and interesting Congress.

The Institution had had a visit in October from M. de Boulard, President of their kindred Society in France, accompanied by two members, who had kindly read papers before a special meeting of the Institution.

Sir John Cadman and the Directors of the Anglo-Iranian Oil Company had generously invited members of the Institution to pay a visit to the well being drilled by the D'Arcy Exploration Company at Portsdown. Over 100 members had taken advantage of this opportunity, on October 10th, and they had been most hospitably entertained by the Company.

The Library had been well maintained, and mention of that side of the Institution could not be allowed to pass without reference to the invaluable work carried out by Mr. G. Sell, who, it was to be regretted, had recently severed his connection with the Institution, after many years of faithful service. Arrangements were at present in hand towards the filling of the vacancy caused by Mr. Sell's retirement and, in the endeavour to make the appointment, it was realized more than ever the splendid work carried out by Mr. Sell.

The Institution was also greatly indebted to the many publishers and members who had presented books and periodicals to the Library.

Mr. Arthur W. Eastlake had continued to fulfil the duties of Honorary Secretary of the Institution, a position he had held from its inception. He had a higher percentage of attendance at all Committee and Council meetings than any other member of the Council. His invaluable help and wise advice were at all times highly appreciated, and of great benefit to the Institution as a whole.

The seven Branches at home and abroad were maintaining a healthy activity and steady progress. That their organizations were appreciated was evidenced by the satisfactory numbers of Branch members referred to above. The Northern Branch, situated as it was in such an important industrial area, had instituted a five-year Course of part-time education in Petroleum Technology, concerned with the production and refining of petroleum and the utilization of its products. This was indeed indicative of a progressive attitude, on which the Council congratulated those concerned.

Reports of the Roumanian and Iranian Branches had not yet been received, due to the fact that their Annual General Meetings would not be held until later in the month. It was hoped that it would be possible to include them in the *Journal*.

A Branch conference, under the Chairmanship of Mr. Dalley, and attended by the Chairmen or Honorary Secretaries of the Burma, Trinidad, Northern, South Wales and Iranian Branches, had been held in London in July, at which valuable suggestions were fully discussed.

A well-attended meeting of members of the Institution in the United States of America had been held in Chicago in November last, at which Messrs. Coxon and Southwell were present, and had addressed the meeting.

Special recognition was due to the Students' Branch (London Section) and its Secretary, Mr. B. C. Ferguson, who was largely responsible for having initiated, on a well-organized basis, joint meetings with the Students of seven other societies located in London. An excellent syllabus of meetings and visits had been issued and, as a general guide and typical of their activities, no less than ten meetings were arranged for the current month.

Such, briefly, was an account of the activities of the Institution during the past year, and he thought that in making that statement he had substantiated the claim that last year had been the most progressive year in the history of the Institution.

He moved the adoption of the Report, and called upon Mr. Dalley to present the Accounts and to second the motion for the adoption of the Report. (*Applause.*)

Mr. C. Dalley, in seconding the motion for the adoption of the Annual Report and Accounts, said that there was no need for him to detain the Meeting with any lengthy remarks. If the position was unsatisfactory from a financial point of view, then considerable explanations became necessary, but on the present occasion, as was the case last year, the financial position of the Institution was very satisfactory.

The Accounts had been circulated, and they called for very little explanation. The Revenue Account showed a surplus of income over expenditure amounting to £268 14*s*. 4*d*. There had been a corresponding surplus last year of £301. This surplus was due to the fact that the income from members' subscriptions and from publications was steadily increasing, whilst the main items of expenditure remained fairly constant. There was one item of expenditure, however, which the members must be prepared to see increased in the future. That was the item of £606 for Rent, Rates and Establishment Charges. The lease of the present premises at Aldine House terminated next June. For the last six months the Council had been examining various alternatives, and everything pointed to the fact that the Institution would have to pay a higher rent for equivalent accommodation in the future. At the moment he was unable to say what would be the position after next June. Members, however, could be assured that the Council was anxious to provide the Institution with better premises than at present. The Council had in mind the ideal of providing members with a dignified house for the Institution where they could enjoy greater facilities than were possible at the present time. In the balance-sheet it would be noted that there was a balance of £1885 available for revenue

purposes. That was a revenue upon which the Institution might have to draw in connection with the furnishing and equipment of new premises.

It would be noticed that the Council had given the Associate Editor an honorarium of £150 on his resignation. He would like to endorse what Mr. Ashley Carter had already said regarding the services which Mr. Sell had rendered to the Institution during his twelve years of association with it. The Council had felt that many members would like to subscribe to a personal gift to Mr. Sell, and an appeal had been issued early in January. The response to that appeal had been very gratifying, and was in itself a testimonial of the appreciation which members had for Mr. Sell's services as Librarian and Associate Editor. It was hoped to make the presentation to Mr. Sell later in the year.

The assets of the Institution were fully detailed on the balance-sheet. The members would note that the investments were all in good sound Trustee securities, of which the market value on December 31 was about £200 more than their cost.

Generally speaking, he thought the financial position of the Institution was quite satisfactory, and he had no hesitation in recommending it to the members of the Institution.

*The motion for the adoption of the Report and Accounts was then put to the meeting by the Chairman and carried unanimously.*

On the motion of Mr. C. E. R. Sams, seconded by Mr. G. W. Gibson, Messrs. Price, Waterhouse & Co. were re-elected auditors for the ensuing year.

The Chairman said that, before proceeding to the next item on the agenda, he wished to digress for a moment. The members were pleased to see with them that evening Mr. Bennion, the Honorary Secretary of the Northern Branch of the Institution, and, in view of that Branch's great activity, he would like Mr. Bennion to supplement the remarks he had made relative to that Branch.

Mr. J. E. Bennion, who was cordially received by the members present, said he understood that the portion of the activities of the Northern Branch which had interested the Council most had been that which had been directed towards the educational benefit of the industry generally. The Committee, after Sir John Cadman's visit, very quickly formed the opinion that the educational facilities in the Manchester University and in the College of Technology were quite inadequate for the educational requirements of the industry. The Committee therefore approached the Director of Education for Manchester with a view to instituting definite petroleum technology lectures. They were somewhat side-tracked by the assertion that the Fuel Section of the College of Technology, and the Chemistry Section, could meet the requirements. After considerable discussion the Director agreed to have a scheme of instruction prepared for consideration by the Committee; unfortunately, these negotiations took some time, and the actual syllabus was printed only a few days before registration of Students was due to take place. Despite this, however, there were now twenty-five students receiving instruction, most of whom

are first-year men. The majority of them are clerks, installation workers and salesmen. He thought that by next year considerable more support would be obtained; there were many inquiries, and he believed the authorities at the College of Technology now realized the value of the subject, and would press forward with the development of specialized instruction for petroleum technologists.

The Northern Branch Committee felt that it was necessary to institute a series of Lectures which would interest the practical salesman and the man who was actually dealing with the product in the market. Mr. E. J. Dunstan, the Refinery Manager of Shell-Mex and B.P. in Manchester, prepared a five years' course on the technology of petroleum more directed to the requirements of the salesman than the type of instruction included in the College five-year course. Mr. Dunstan had taken as the first year a general survey of the industry, with an explanation of the chemical and scientific tests. The matter would be amplified in the second year; the third year was to be devoted to an explanation of the scientific testing of petroleum, and in the fourth year the application of these tests to the production, selection and use of petroleum products in industry would receive treatment. The fifth and final year would be devoted to the subject of lubrication and lubricants.

The membership of the Branch seemed to have surprised some members of the Institution. The reason why the Branch had such a large number of members was that it had not insisted on academic qualifications; the only qualification it needed was that the applicant for membership should be engaged in the industry. The majority of the members were salesmen, and it was rather significant to find that most of them were salesmen in the smaller oil companies. They appeared to appreciate the fact that they could not get any instruction elsewhere. He thought the Branch had also been able to attract a few people to the membership of the parent Institution.

THE CHAIRMAN then invited questions or remarks on the Report and Accounts, but none was forthcoming.

## INDUCTION OF PRESIDENT.

THE CHAIRMAN said it was then his very pleasurable duty to announce the unanimous choice by the Council, and the acceptance of the Presidency of the Institution in succession to Sir John Cadman, of Lt.-Col. S. J. M. Auld. Lt.-Col. Auld, by reason of his scientific attainments, was well known not only to members of the Institution, but to many connected with science and the petroleum industry in this and other countries where petroleum played such an important part. Lt.-Col. Auld's connection with the Institution dated back to 1920. Five years ago he had been elected a member of Council. This had been quickly succeeded by his election as a Vice-President, and now he had had conferred upon him the charge of the destinies of the Institution. There were few, if any, scientists with such a versatile practical knowledge and experience as those possessed by Lt.-Col. Auld.

Lt.-Col. Auld had always had a special interest in hydrocarbons. His

first position after graduating from Würzburg had been with an old-established firm of tar distillers. Thereafter he had been claimed by biological chemistry, and then by agriculture. The thesis which had earned his degree of Doctor of Science in the University of London had dealt with the nature and action of unorganized ferments, and similar work had occupied him until the War, by which time he had attained the position of Professor of Agricultural Chemistry at University College, Reading, this being the first Chair of Agricultural Chemistry established in the country.

After the War, Lt.-Col. Auld had returned to industry and his older interests, by accepting a position with the Anglo-Iranian Oil Company, with whom he had remained for some nine years. His work had been chemical engineering in character, and had taken him on behalf of the Company to Burma, Persia and Iraq. Although his work in cracking was well known, it might be considered that his pioneering survey of the gas production of the main Masjid-i-Sulaiman field was amongst his best achievements. This survey had initiated the control of the enormous production of natural gas in Iran, which had led to its recovery and exploitation. Some account of the work was published in the Institution's *Journal* for 1928.

Following a period of a few years in private practice—years during which Lt.-Col. Auld had been associated with some of this country's leading industrial enterprises—he had joined the Vacuum Oil Company, Ltd. He had been later appointed their Chief Technologist, the position which he now held. In the broadest sense, his duties were responsibility for the products of the Company, involving all matters of technical development. The scope of his work in lubrication was, perhaps, best indicated by his recent papers, that on "Characteristics of Solvent Refined Motor Oils" having been read before the Institution, and that on "The Susceptivity of Mineral Lubricants in Use" having been read before the Society of Chemical Industry. He was the author of several scientific and technical works and publications.

Lt.-Col. Auld had had a most distinguished war service. He had first served with his regiment, but the Government had decided that talents such as those possessed by Lt.-Col. Auld could be more usefully employed technically. He had therefore been appointed Chemical Advisor at G.H.Q., and Deputy Assistant Director of Gas Services between 1915 and 1917. Perhaps his most responsible task during the War had been his leadership of the British Army's Gas Warfare Mission to the United States, which country had honoured him by bestowing on him the American Distinguished Service Medal. He had been mentioned in despatches, and awarded the Military Cross. The British Government had further recognized his services by conferring on him the Order of the British Empire. Lt.-Col. Auld was still on the Regular Army Reserve of Officers, and it was but a few months ago that he delivered an excellent address on gas in warfare.

Lt.-Col. Auld, in addition to serving on various committees, was selected by the Institution as Chairman of the Engineering Standardization Committee. In this direction he was prominently connected with the British Standards Institution. Lt.-Col. Auld had always thrown himself whole-

heartedly into the advancement of the Institution, and they had every reason to congratulate themselves on his acceptance of the Presidency, whereby the Institution was assured of a continued progress under his able guidance.

He therefore now asked Lt.-Col. Auld to occupy the President's Chair.

(*Lt.-Col. Auld then took the Presidential Chair amid the acclamation of the members present.*)

THE PRESIDENT (Lt.-Col. S. J. M. Auld) thanked Mr. Ashley Carter for the manner in which he had inducted him into the Presidential Chair. In the enforced absence of the immediate Past-President, Sir John Cadman, he assured the members that he could think of no one whom he would have preferred to convey that dignity to him.

He wished to thank those present for the manner in which they had received, and supported the things said about him by Mr. Ashley Carter.

But for all the eulogia it was with a humble mind and a deep feeling of unworthiness that he entered into his term of office. The standard expected of its President by the Institution was high. The standard which had been maintained by his predecessors had been high. That had especially been the case regarding Sir John Cadman.

Sir John, the acknowledged leader of the British Oil Industry, eminent amongst administrators as in the technical world, active in other great spheres of industry and commerce, yet had made the time to act in the fullest manner as President of the Institution.

Sir John's wise guidance, coupled with his belief in the value and in the future of the Institution, had left a mark which it was hoped would long remain. As the head of one of the biggest oil groups in the world it was stimulating to their own activities to find that Sir John realized and appreciated the big debt which the industry owed to the I.P.T. If he himself could see that that feeling was held and strengthened he would be satisfied.

All he could say was that he would do his utmost to uphold the honour and dignity of the Institution, and to maintain its high standing amongst the learned societies of the country and its reputation in the outside world.

His forthcoming year as President was likely to be an important one. It would cover the Second World Petroleum Congress, which was to be held in Paris in June. There would be seen therein a continuance of the work started by the Institution of Petroleum Technologists three years ago. The Institution looked forward to active participation in the Congress and to an outcome equally successful to that achieved in 1933.

In the second place, it was likely that the Council would shortly ask permission from the members of the Institution to seek powers to modify the Articles and Memorandum of Association. It had been felt for some time past that the Institution could better perform the functions for which it was originally founded by enlarging the scope of its activities and broadening the basis of its membership. Nothing would be suggested which would detract from the position of the Institution as the ruling professional body connected with petroleum, but it was wished to keep abreast of the many

new interests which had arisen and to act as leader in their co-ordination and control. He felt that the suggestions which would be placed before the Institution would meet with its entire approval.

In conclusion, he wished to thank the Institution as a whole, as he had already thanked the Council, for the great honour which had been accorded him by being elected as the new President.

## Presentation of the Redwood Medal to Mr. H. R. Ricardo.

The President said that the first duty he had to perform as President of the Institution was a very pleasurable one. It was to present the Redwood Medal to Mr. H. R. Ricardo. (*Applause.*)

The Redwood Medal had been established in 1921 in honour of the Founder-President of the Institution. The terms of its award had been modified in 1931, whereby the Institution should be free to confer this, its highest award, on men of science with a distinguished record of achievement, untrammelled by previous conditions of publication or otherwise.

The present conditions were "The Redwood Medal shall be awarded as and when desirable, but not more than once in each year, to a petroleum technologist of outstanding eminence, irrespective of nationality or membership of the Institution."

Since its original foundation until to-day the Medal had been presented only five times. Since the modified terms of award were adopted it had been presented twice: in 1932 to Dr. Edeleanu and in 1934 to Dr. David White.

It was an award which was not easily won. The qualifications required were exceptional. He could assure the members, however, that the recommendation by the Awards Committee, and the decision by the Council of the Institution, to award the Redwood Medal to Mr. H. R. Ricardo, had been made unanimously and, indeed, enthusiastically.

To the members of the Institution of Petroleum Technologists, as to all concerned with the design and operation of the internal-combustion engine, Mr. Ricardo's name was a household word. No consideration could be given to the method of operation of combustion within the engine without reference to his work.

Mr. Ricardo had made some of his earliest observations on the occurrence of detonation in the internal-combustion engine whilst still at Cambridge, in Hopkinson's laboratory. Apart from "spare-time" work, however, it was not until the years of the War, when he had become Consulting Engineer to the Mechanical Warfare Department, that he had been enabled to study the question deeply and to apply his results to the design of petrol engines. Following post-war research for the Air Ministry, he had carried out at the instigation of the Asiatic Petroleum Company, Ltd., from 1919 onwards, intensive investigation into the relationship of fuel constituents to the engine compressions which they would stand. The results of this justly celebrated work and the conclusions reached had been published and re-published between 1921 and 1928.

That work had laid the foundations of their knowledge of the action of fuels in homogeneous charge engines, particularly with regard to detonation. The conception of octane rating of fuels was almost entirely based on Mr. Ricardo's work.

In 1928 Mr. Ricardo had been elected a Fellow of the Royal Society. In the same year he had read before the Institution a paper entitled "Mechanical Design in Relation to Detonation."

In the following year he had been elected an Honorary Member of the Institution.

Mr. Ricardo had been honoured for his work in succession by the North-East Coast Institution of Engineers and Shipbuilders; the Royal Aeronautical Society; the Institution of Automobile Engineers; and the Institute of Fuel.

In conferring the Institution's highest award upon Mr. Ricardo, the members felt that they were paying a tribute to one whose work had been outstanding in advancing knowledge and practice in the Technology of Petroleum.

No words of his could add to the honour which the Institution of Petroleum Technologists wished to confer upon Mr. Ricardo by the presentation of the Medal.

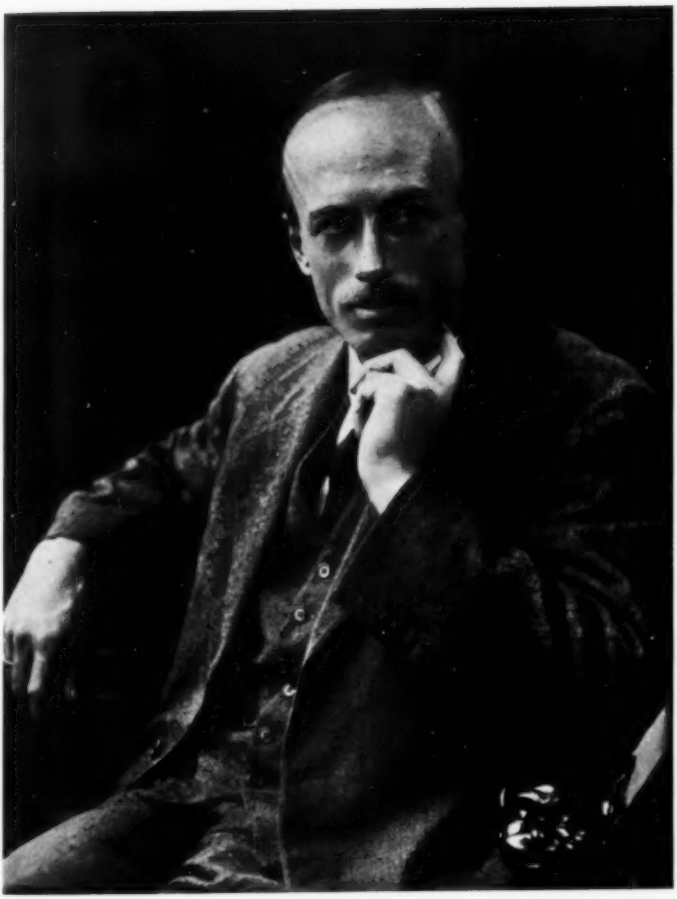
On behalf of the Institution he handed Mr. Ricardo the Redwood Medal, and wished him many years wherein to continue to add to the world's store of knowledge. (*Prolonged applause.*)

MR. H. R. RICARDO in acknowledging the presentation, said :—

I need hardly tell you how flattered I feel at all the kind things which the President has said, and at being awarded the much-prized Redwood Medal, an honour that I shall treasure all my life. I am conscious, however, of enjoying the benefit of reflected glory and the reward of having talked much and often on the subject of detonation.

I think we all agree to-day that, so far as petrol is concerned, the one vital issue is the tendency of the fuel to detonate. Until about twenty years ago in this country, and until much more recently in America, detonation was believed to be merely a noisy form of premature ignition, and the remedy was sought not in the make-up of the fuel, but in the better cooling of the cylinder. This helped, but only a very little. The trouble was with us all the time, and any treatment designed to remove pre-ignition tended also to reduce detonation; thus there was some, but, looking back, only a little, excuse for confusing these two really quite independent nuisances.

I think that the whole credit for the discovery of detonation as a phenomenon, quite distinct from pre-ignition, is due to the late Professor Hopkinson, a man of quite outstanding brilliance, but unfortunately of very few words, and still fewer writings. I had the good fortune to be first a pupil of and later an assistant to Professor Hopkinson at Cambridge. At that period—more than thirty years ago—Hopkinson was developing, among other things, an optical indicator for high-speed engines, and it fell to my lot to assist in this particular problem. The indicator embodied a very small piston which operated against a flat spring to which was attached a mirror. I will not go into all the difficulties, mechanical and otherwise, which we encountered in the early stages, but eventually we got it to work very well. We tried it on a high-speed steam engine, and it gave very plausible-looking diagrams. We tried it on a gas engine, and it did the same. Lastly, we tried it on a petrol engine, and still it did the same, so



HARRY R. RICARDO, F.R.S.
*Redwood Medallist, 1937.*

[*To face p.* 308.

UNIV. OF MICH.

long as the engine was not knocking. Immediately the engine started to knock, away flew the mirror, and no attachment that we could devise would persuade it to stay put. The mirror did not just work loose—it flew half across the room, and my recollection of those days is that we spent the bulk of our time crawling about on hands and knees searching the floor for mirrors. I, like everyone else at that time, attributed the trouble to pre-ignition, but Hopkinson would have none of this. He pointed out that pre-ignition could produce no such sudden pressure rise as would be required to flick the mirror half across the laboratory. With his characteristic prescience, Hopkinson put his finger on the spot straight away, and ascribed the shock to the impact of a detonation wave against the piston of the indicator.

This was more than thirty years ago, and more than ten years before the existence of detonation was recognized by others. Hopkinson's jumping mirror was at least fifteen years ahead of Midgley's bouncing pin, and much more effective as a knock-meter. As a profound admirer of Hopkinson I followed his teachings, and so have got away with much of the glamour and reward which should have been his.

## Vote of Thanks to Sir John Cadman.

Mr. Kewley said it was difficult to express adequately what the Institution owed to Sir John Cadman for all he had done for it, not only in the early years when Sir John had been one of its earliest Presidents, but particularly also during the last two years. During this period the members had been able to see for themselves so much of Sir John's activities on their behalf that it would appear redundant for him (Mr. Kewley) to reiterate them. The Report which the Members had just passed well showed the effect of Sir John's influence on the rate of progress of the Institution. Members of the Council had been able to see a little more of Sir John than had the ordinary members, so that they had had an even better opportunity of appreciating his full value. Sir John had been very regular in his attendance at Council meetings. He had made a model Chairman. He had combined firmness with tact—which was so often necessary in handling a rather large Council such as theirs—and he had added at the same time to the meetings just that little touch of informality which had made the Council meetings happy and enjoyable. Sir John had been always concise and to the point, and had had an extraordinary grasp of the real points at issue. When these tended in the course of a long discussion to become obscured, Sir John had always brought those present back to the point. His great interest in the Institution had been displayed by the fact that he had paid a visit to Manchester to open the Northern Branch. On that occasion the Lord Mayor and the President of the Manchester Ship Canal Co. expressed their admiration at the power which the Institution of Petroleum Technologists wielded, in that it was the only body who had ever been able to persuade Sir John to visit Manchester. He was sure that as a past-President Sir John would enhance the reputation of his fellow past-Presidents, and would continue to take an interest in the affairs of the Institution—an interest that would remain real and lasting. He asked the members to thank Sir John for all that

he had done for the Institution during his long period of association with it.

Mr. C. Dabell seconded Mr. Kewley's remarks, and desired also, on the members' behalf, to thank the members of the Council for their honorary and very much appreciated efforts during the past year.

*The vote of thanks was carried by acclamation.*

*The meeting then terminated.*

# EXTENDED VAPOUR-PRESSURE CHART FOR HYDROCARBONS AND PETROLEUM PRODUCTS.

By E. S. L. Beale, M.A., F.Inst.P. (Member).

SYNOPSIS.

The Boiling-Point Conversion Chart previously published in this *Journal* (Beale and Docksey, Vol. **21**, pp. 860–870, Oct. 1935) has been extended to cover pressures above atmospheric for the estimation of vapour pressures in fractionating column calculations. A modification of the same chart is given to show how it can be used for adjusting the boiling point of residues from crude oil for small pressure changes, as is required in the calculation of equilibrium temperatures.

## Introduction.

The Boiling-Point Conversion Chart given by Beale and Docksey (*loc. cit.*) was primarily intended for the conversion of the boiling points of petroleum fractions of narrow boiling range to atmospheric pressure from pressures below atmospheric as determined by distillation analysis, more particularly in the case of high-boiling fractions which must be distilled at low pressures in order to avoid thermal decomposition.

Previously published charts had been found to be somewhat unreliable, particularly in the region of 10 mm. of mercury absolute, and below. This chart has had a considerable degree of acceptance, and the usefulness of this type of nomogram for the estimation of the vapour pressures of fractions in column calculations has become apparent.

For this purpose, of course, not only low vapour pressures, but also high vapour pressures, must be shown on the chart.

## Extension of Pressure Scale.

The pressure scale on the original chart was limited to 760 mm. mercury. It was therefore necessary to extend the pressure scale to include higher pressures as well as pressures below atmospheric. This has been done by the same method as used in the construction of the chart mentioned above—namely, by plotting the same and other available data first as a Vapour-Pressure–Temperature chart on a scale of $\log p - \frac{1}{T^\circ \text{ abs.}}$. The results from this chart were then cross-plotted in the form of a chart giving boiling point at $p$ mm. against boiling point at 760 mm. (Fig. 4 in previous paper). From these charts the pressure scale can be extended up to the limit of the available data—namely, the critical pressure.

For the purpose of column calculations, it is well known that a useful approximation of the vapour pressure of a cut of wide boiling range containing some very light components can be obtained by assuming that these lighter components behave as if they had the vapour pressures given by the extrapolation of the vapour-pressure curve *beyond* the critical point.

Granted this assumption, the extrapolation can quite simply be done

without much ambiguity, because the vapour-pressure lines plotted on the scale of $\log p - \frac{1}{T° \text{ abs.}}$ are very nearly straight, and can therefore be extrapolated with confidence over a small temperature range. This has been done in the construction of the extended chart shown in Fig. 1, which has been taken up to 100,000 mm. of mercury, or 2000 lb. per sq. inch, although the critical temperature of most hydrocarbons is below 1000 lb. per sq. inch.

## Extension of Temperature Scales.

For similar reasons, when estimating vapour pressures of fractions for column calculations, it is often necessary to use a figure for the vapour pressure of fractions having boiling points at 760 mm. beyond the limits given on the previous chart, as this was confined to the range 100° C. to 700° C. This scale has therefore been extended to cover the range −100° C. to 1000° C.

With regard to the low-temperature end, it is more usual to make use of actual fractions obtained from distillation analysis for the low-boiling constituents, such as pentanes, butanes, etc., boiling at 36° C. and 0° C., respectively, in which case the vapour-pressure data for the appropriate pure hydrocarbon would be used, but as an approximation the new chart can be used with fair accuracy down to 0° C., and for some purposes it may be useful below 0° C. also, but in this region it can only be regarded as a rough approximation.

With regard to the high-temperature end of the boiling-point scale, it is now generally realized that in many crudes there is a substantial quantity of extremely high-boiling material, extending well above 700° C. b.p., and the vapour pressure of these must be estimated when making equilibrium flash or fractionating-column calculations, in the case, for instance, of the production of pitch from asphaltic crudes.

The temperature scales on this chart are uniform owing to the fact that the lines of constant pressure on the boiling-point conversion graph (b.p. at $p$ mm. to b.p. at 760 mm.) are straight, as shown in Fig. 4 of the previous paper. A slight amount of curvature is noticeable at the lowest temperatures and pressures (below 0° C. and 1 mm.). However, at high temperatures these lines are almost perfectly straight, and therefore the boiling-point scale can be extrapolated with confidence in the direction of high temperatures.

## Comparison with Previous Chart.

On the new chart, Fig. 1, it will be seen that the pressure scale is straight over the range 1·0 mm. up to the maximum pressure, 100,000 mm., whereas on the previous chart there was a certain amount of curvature. It would appear at first sight that this change of scale-shape would represent a substantial modification in the data on which the chart is based, and that it would give considerably different values for the vapour pressure or the converted boiling point. However, this is not the case, as can readily be proved by converting the boiling points by these two charts in this range, and it will be found that the change amounts to no more than about

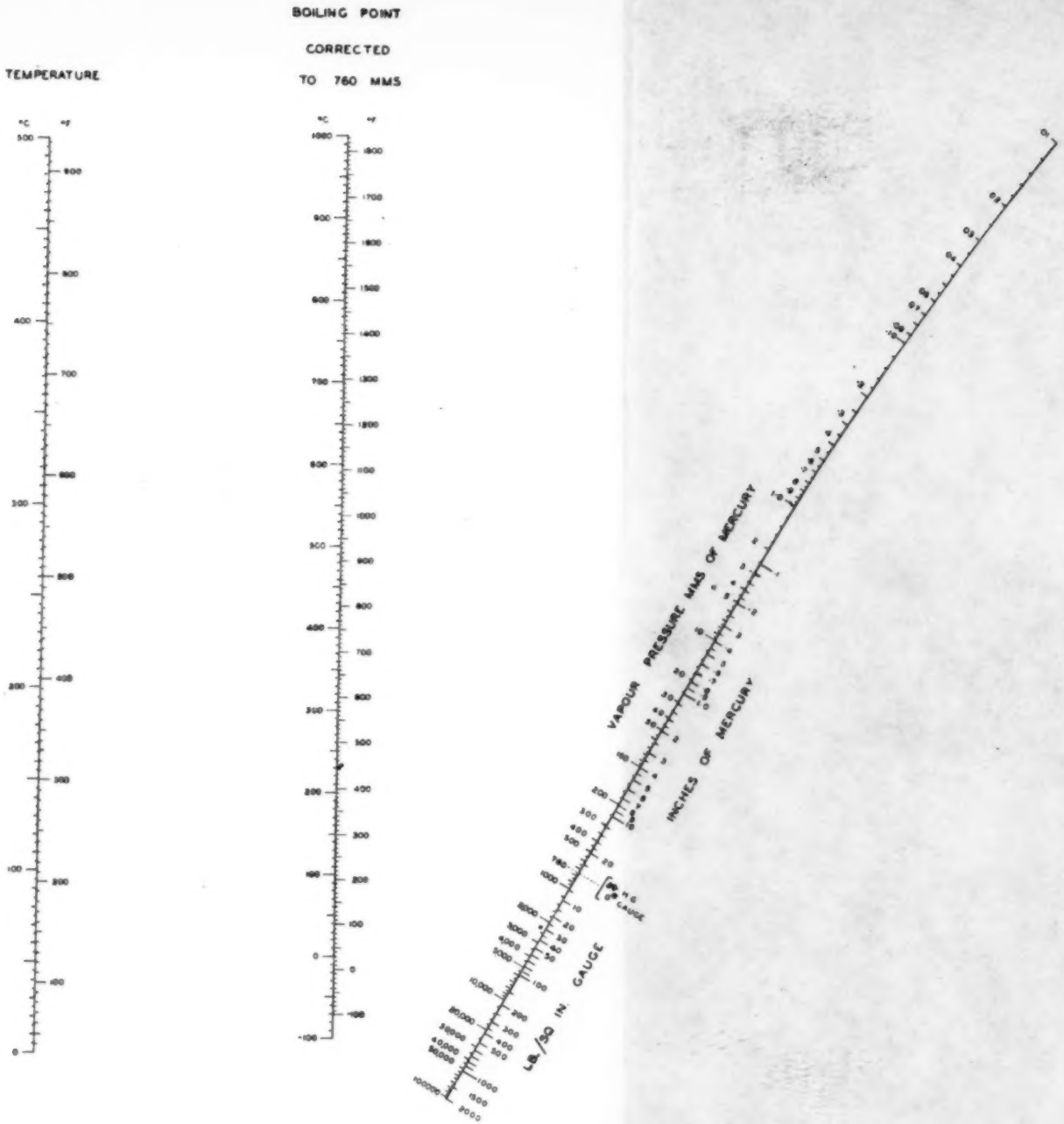



FIG. 1.

VAPOUR-PRESSURE CHART FOR NARROW CUT PETROLEUM PRODUCTS.

[To face p. 312.

UNIV. OF MICH.

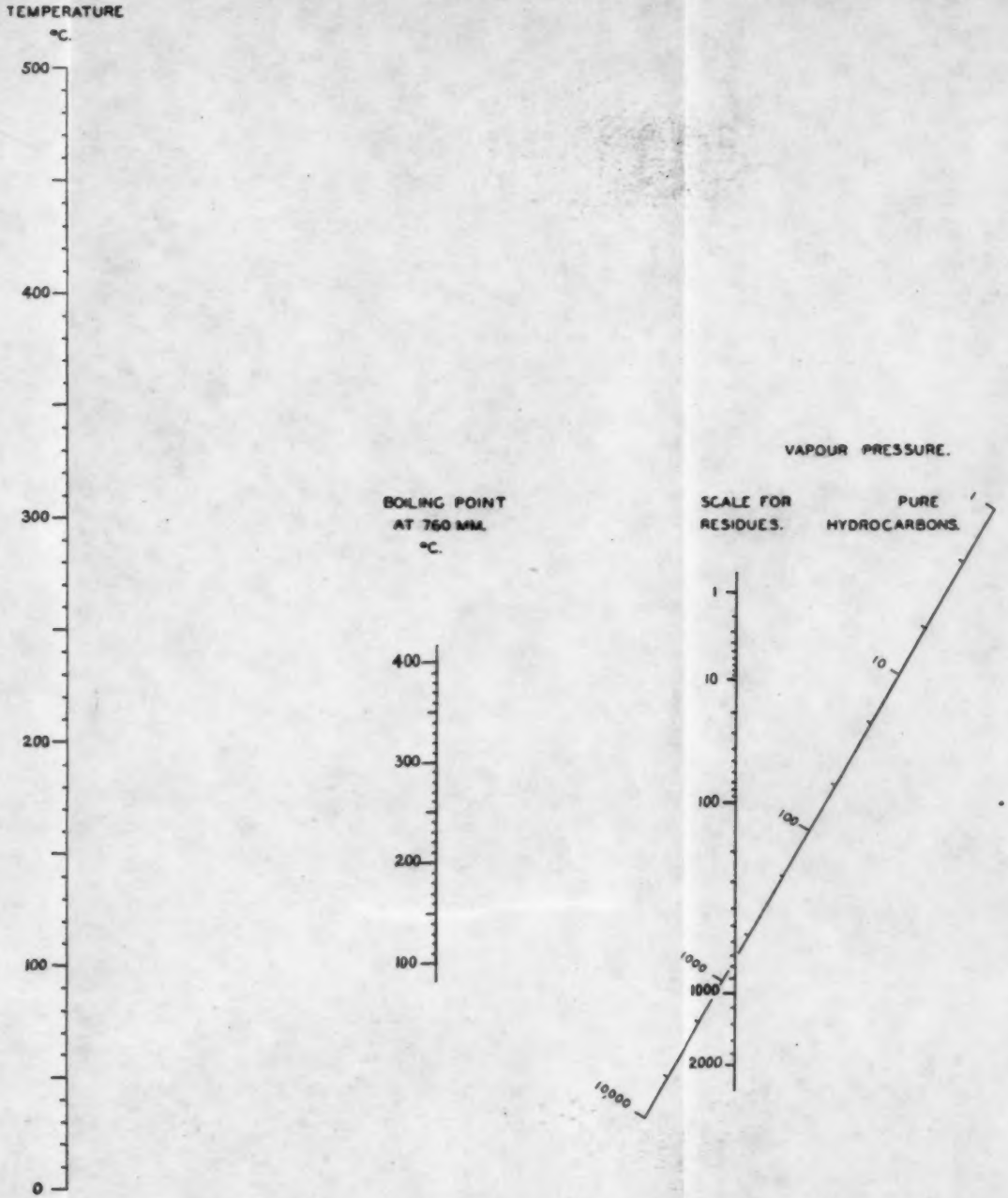



FIG. 2.

VAPOUR-PRESSURE CHART FOR RESIDUES.

UNIV. OF MICH.

1° C. at any point. As the accuracy claimed for the original chart was only ± 2° C. and the boiling-point scales can only be read to this accuracy with difficulty, the difference between the old and new charts can be said to be negligible.

The reason for the change in scale-shape was due to the fact that, although the old scale was the best representation of the data up to 760 mm., when the scale was drawn to cover the whole pressure range it was found that the pressure scale above 760 mm. was accurately straight, and that the best representation of all the data was a straight scale from the highest pressure down to 1 mm.

As mentioned above, it was found that the effect of the change in position of the intermediate divisions was so small as to be negligible, and in all probability the new scale represents the data rather more accurately than the original scale.

### Modification of Chart for Residues.

When calculating equilibrium temperatures in a fractionating column, the method usually adopted is to calculate the partial pressure of each fraction in the mixture at a temperature which is estimated to be close to the true equilibrium temperature. The sum of the partial pressures of all the fractions gives the vapour pressure of the mixture at the estimated temperature. As this vapour pressure will not be exactly equal to the actual pressure in the column at the point under consideration, it is necessary to adjust the boiling point of the mixture over a relatively small range of pressure to obtain the equilibrium temperature at the actual pressure in the column.

This conversion of boiling points can be done quite accurately enough by means of the vapour-pressure chart described above, when the mixture under consideration has a reasonably narrow boiling range, as, for instance, in the case of liquids on the trays above the feed plate of crude topping units. However, in the case of a liquid in the well of a stripper of a crude topping unit, the boiling range is very wide, as it corresponds with a residue on the crude charged to the column. It is, of course, well known that the slope of the vapour-pressure lines of such residues is not the same as that of narrow-cut fractions or pure hydrocarbons, and therefore the normal vapour-pressure chart cannot be used with any accuracy for converting boiling points of such residues. To save the labour of recalculating the vapour pressure of such mixtures at temperatures successively closer to the true equilibrium temperature, it is very useful to have a boiling-point conversion chart which can be used for this purpose. For any given crude such a chart can be provided by a modification of the pressure scale on the vapour-pressure chart for hydrocarbons. A typical scale which has been derived from the vapour-pressure data obtained experimentally on various residues from a mixed-base crude is shown in Fig. 2. This chart may be regarded as reasonably typical of crude oils having a true boiling-point curve reasonably similar to the one for this particular crude given in Fig. 3. The vapour-pressure curves from which this pressure scale is derived are given in Fig. 4.

It will be observed that in this case the pressure scale happens to lie

parallel to the boiling-point scales, but this, of course, is a coincidence. It will also be found that the pressure scale for residues gives very nearly the same vapour pressure at all temperatures for a residue having a boiling point at 760 mm. of 375° C. This is an expression of the fact that the slope of the vapour-pressure curve for this residue was found to be very nearly the same as that for pure hydrocarbons having the same boiling point.

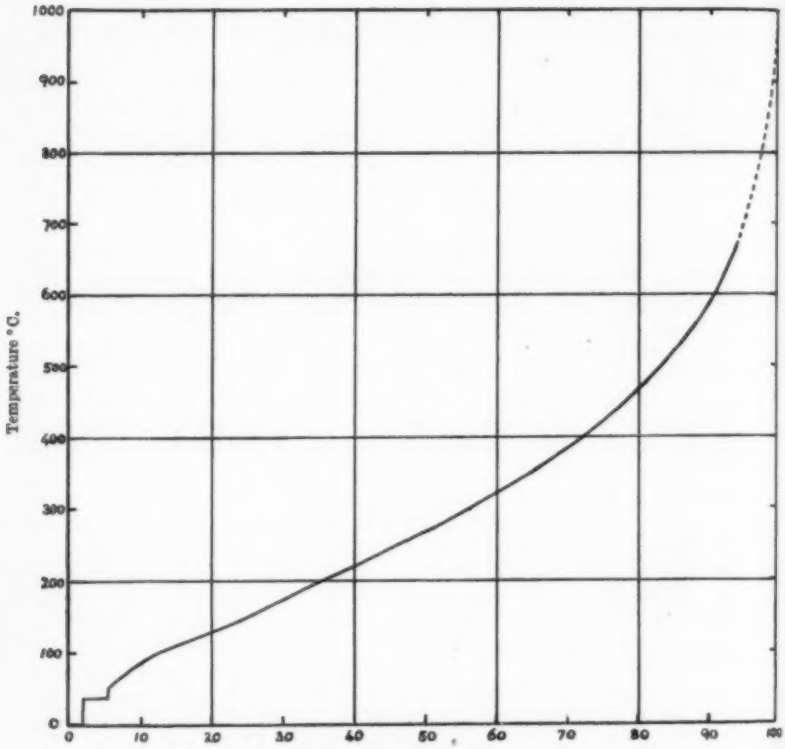



FIG. 3.

T.B.P. CURVE OF MIXED BASE CRUDE.

Residues having a lower boiling point than this were found to have a substantially smaller slope, as shown in Fig. 4. Residues with boiling points higher than about 400° C. were found to agree more closely with the pressure scale for pure hydrocarbons than with the scale for the lighter residues. For this reason, the scale of boiling point at 760 mm. has only been carried up to 400° C. in this case.

The pressure scale for crudes having a different composition would, of course, be different, but it is probable that the scale would also be straight

as in this case, and that the residue having a boiling point not very far removed from 400° C. would have a vapour-pressure curve with nearly the same slope as the pure hydrocarbons having the same boiling point, in which case the divisions on the pressure scale for these residues could be put on the pressure scale in a similar way to that shown in Fig. 2—namely, by drawing a set of straight lines radially from the point of the scale of boiling point at 760 mm. marked 375° C. or, say, 400° C.

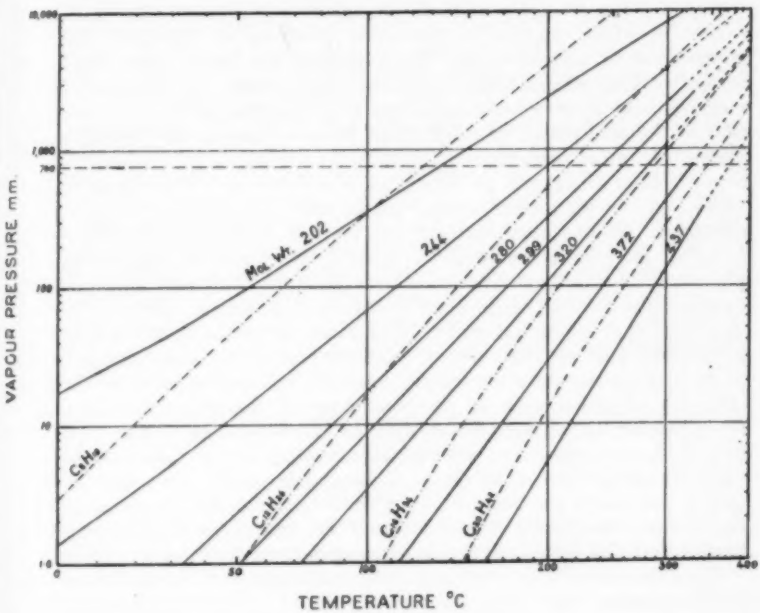



FIG. 4.

VAPOUR PRESSURES OF RESIDUES FROM MIXED BASE CRUDE.

The direction for the new pressure scale for residues for any given crude can easily be determined on these assumptions by calculating the vapour pressure of a low-boiling residue at a comparatively low temperature, *i.e.* such as to give a vapour pressure of about 10 to 20 mm., say. This will give an intersection on the required scale with the line drawn from 400° C. on the boiling point at 760 mm. scale to the same pressure on the scale for hydrocarbons.

Since all pressure scales must obviously pass through the same point at 760 mm., the direction of the new pressure scale will thus be fixed.

# THE DESIGN AND ANALYSIS OF FRACTIONATING COLUMNS FOR COMPLEX MIXTURES.

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## Introduction.

The problem of design and analysis of the performance of fractionating towers in which complex hydrocarbon mixtures are distilled has been approached in several ways. Consideration has been given chiefly to towers working continuously, as opposed to batchwise, and all the acceptable methods have as their bases equations which are derived from a consideration of the attainment of equilibrium between vapour and liquid on the plates. In most cases the equilibrium is assumed to be perfect, and the tower is then considered to consist of a number of "theoretical plates" which can be reduced to actual plates from a knowledge of the plate efficiency. In one case—namely, the method of Lewis and Wilde [5]—the fact that the plate is not perfect is allowed for by the adoption of the Murphree efficiency in the derivation of the equation. The resulting equation is excellent for the analysis of plate performance if sufficient data are obtainable from the test on the tower. This must include not only true boiling-point curves or (in the case of stabilizers) accurate compositions of the products from the tower the separation of which is used to calculate the plate efficiency, together with an accurate value of the reflux ratio, but also temperatures on all the plates used in the separation. The latter are frequently not capable of determination, owing to the failure to provide thermometer pockets on all plates in commercial units. In a case in which only a few plates are being used for the separation, the temperatures can be obtained roughly by interpolation if the values for the end-plates are known, but this procedure is not very satisfactory.

The Lewis and Wilde equation is extremely laborious to apply to design. Some attempts have been made to simplify the procedure by adopting a graphical method, but these either fail on account of a failure to understand the true intricacy of the problem, or give only approximate solutions. Thiele and Geddes [8] succeeded in evolving a method of design based on the direct use of this equation, but it is still laborious, and, furthermore, needs considerable experience of the temperature variation from plate to plate for its successful application.

The necessity of estimating the plate temperatures accurately during the course of the calculation is the reason for the lack of success to be attained in the application of the Lewis and Wilde method to design. This can be overcome by making use of the fact that the ratio of the vapour pressures of two hydrocarbons (that is, the relative volatility) is reasonably constant over a wide temperature range. In this way Fenske [3] derived an equation applicable to a tower working under total reflux. Underwood, in the course of his authoritative review of fractionation in general,[9] extended the relative volatility ratio method to give an equation applicable to finite reflux ratios. Underwood briefly shows how the equation may be used to give a workable stepwise calculation of the separation between overhead

and residue in a stabilizing column in which the feed is correctly placed, and in which the separation between two components is relatively complete. No details of the difficulty of application to actual design are given. This equation is adopted in this paper as the basis of the tabular stepwise calculation applicable to what may be called continuous mixtures (*i.e.* in which the pure components cannot be distinguished), which is given later.

The relative volatility concept has also been used by Underwood in his "enrichment factor" method,[10] again applicable to stabilizers in which the feed is correctly placed. The method is admittedly an approximation, but is excellent for the design of stabilizers containing a large number of plates, since it does not involve any stepwise calculation. An approximate method with similar applications and advantages is the absorption factor method of Brown and Souders.[2]

It will be seen from this brief and by no means exhaustive review that, for design, attention has been paid chiefly to methods the main usefulness of which lies in their application to stabilizers. For towers used for distilling continuous mixtures only methods of an approximate and empirical nature have been proposed, with the exception of that of Thiele and Geddes.

Analysis of fractionating towers to give the plate efficiency can be carried out by using the Lewis and Wilde equation if sufficiently accurate data are available. Analysis has also been made by means of approximate and empirical methods, but such analyses are useful rather as a check on the applicability of the method to design than for the purpose of determining plate efficiencies.

## PART I.—DERIVATION OF EQUATIONS AND METHOD OF CALCULATION.

### Introduction.

The calculation of the products which will be obtained when a given feed is fractionated under known conditions is a problem which is capable of an unique solution. No rigorous method has been evolved, however, which allows this solution to be obtained for complex mixtures without recourse to a series of approximations. The calculation is bound to be based on some assumption of the physical action taking place in the tower, that already referred to (attainment of equilibrium on a plate) being a widely accepted one. It is adopted as the basis of calculation in this paper.

If the equilibrium on each plate is perfect and Raoult's Law holds, the Lewis and Wilde equation expressed in the symbols used later becomes :—

$$a_n = \frac{\pi}{P_n^a}\left[\frac{O_{n-1}}{V_n}a_{n-1} + \frac{D}{V_n}A_d\right]$$

$a_n$ = Mol fraction of component $A$ on plate $n$.
$a_{n-1}$ = Mol fraction of component $A$ on plate $n-1$ next above $n$.
$A_d$ = Mol fraction of component $A$ in distillate.
$O_{n-1}$ = Total mols. of liquid falling from plate $n-1$.
$V_n$ = Total mols. of vapour rising from plate $n$.
$D$ = Total mols. of distillate.
$P_n^a$ = Vapour pressure of component $A$ at temperature of plate $n$.
$\pi$ = Total pressure above plate $n$.

Supposing now that in a tower in which the reflux ratio is known we know the *exact* composition of the liquid at some point. Then, by means of the equation, we can calculate the composition at a point one plate farther down the column. The procedure is to assume a value for the temperature of the plate, thus fixing values of the vapour pressures of all components, and to work out the mol fraction of each component. These mol fractions should, if the assumption for the plate temperature is correct, add up to unity. If they do not do so a fresh assumption for the temperature must be made. Thus, each step will involve a series of approximations, and added to this is the difficulty that when designing a tower the exact composition cannot be predetermined at any point. Thus, knowing the composition of the feed, and the number of plates and reflux ratio to be used in the separation, we should have to proceed as follows :—

A composition for the distillate is assumed. This can be made approximately correct, but not exact. A stepwise plate-to-plate calculation is then made from the top of the column to the bottom, thus obtaining the calculated composition of the residue. Each step will involve a series of approximations. But since we know the composition of the feed and the quantity and composition of the distillate which has been assumed, we can straightway obtain the assumed composition of the residue by difference. This should be identical with the composition of the residue as calculated by the stepwise procedure if the initial assumption for the distillate has been correct. If the two residues compositions do not agree, a fresh assumption for the distillate must be made, and the process repeated.

Clearly, making the calculation in this way would be impracticable, on account of the excessive labour involved. It is possible, however, to get rid of the series of approximations which have to be made at each step, by introducing the assumption that the ratio of the vapour pressures of two hydrocarbons may be considered constant over a temperature range which is wide enough to cover a reasonable section of the tower. This assumption is not novel, and while it introduces some inaccuracy into the calculation, the inaccuracy is negligible if the values of the ratios of the vapour pressures of the various components, or the volatility ratios, as they are usually called, are made correct at the mean temperature of the section of the tower under consideration.

The necessity for making an initial assumption for the composition at some point in the tower, and for correcting this assumption by a series of approximations, remains.

In this paper we shall first of all evolve methods of making the plate-to-plate calculations in both rectifying and stripping sections of a tower working on the continuous principle, in tabular form convenient for calculation. These will rest on the conventions that perfect equilibrium is attained on each plate, and that constant volatility ratios can be used without loss of accuracy. The tabular calculation allows compositions of liquids on the trays in the rectifying section to be calculated, proceeding from the top downwards, and of vapour rising from trays in the stripping section from the bottom upwards. The application of these tabular calculations to analysis of tower performance or to design depends on the composition being either known or assumed at one point in the tower. Plate-to-plate

## Symbols.

The following symbols have been used throughout :—

| | |
|---|---|
| $a\ b\ c\ d.\ \ldots\ldots$ | Molecular fractions of components in the liquid at any point in the column. Each letter represents a pure substance, and the boiling points increase from $a$ to $d$. |
| $A\ B\ C\ D.\ \ldots\ldots$ | Molecular fractions of components in the vapour. |
| $F.$ | Mols of feed per unit time. |
| $D.$ | Mols of distillate per unit time. |
| $W.$ | Mols of residue per unit time. |
| $n.$ | As a suffix, refers to the $n$th plate from the top in the rectifying column. |
| $\overline{m}.$ | As a suffix, refers to the $\overline{m}$th plate from the bottom in the stripping column. |
| $d,\ w,\ f.$ | As a suffix, refers to distillate, residue and feed. |
| $P^a_n P^b_n.$ | Vapour pressures of components at temperature of $n$th plate. |
| $\pi.$ | Total pressure in column. |
| $\alpha_a\ \alpha_b\ \alpha_c\ \alpha_d.$ | Relative volatilities, = vapour pressure of component $a$, $b$, $c$, etc., divided by vapour pressure of reference component. (All vapour pressures taken at the mean temperature of the column.) |
| $O_n.$ | Mols of liquid falling from plate $n$ in unit time. |
| $V_n.$ | Mols of vapour rising from plate $n$ in unit time. |
| $a^*$ | Mol proportion in liquid. For definition see equation (9), page 320. |
| $A^*.$ | Mol proportion in vapour. For definition see equation (17), page 322. |

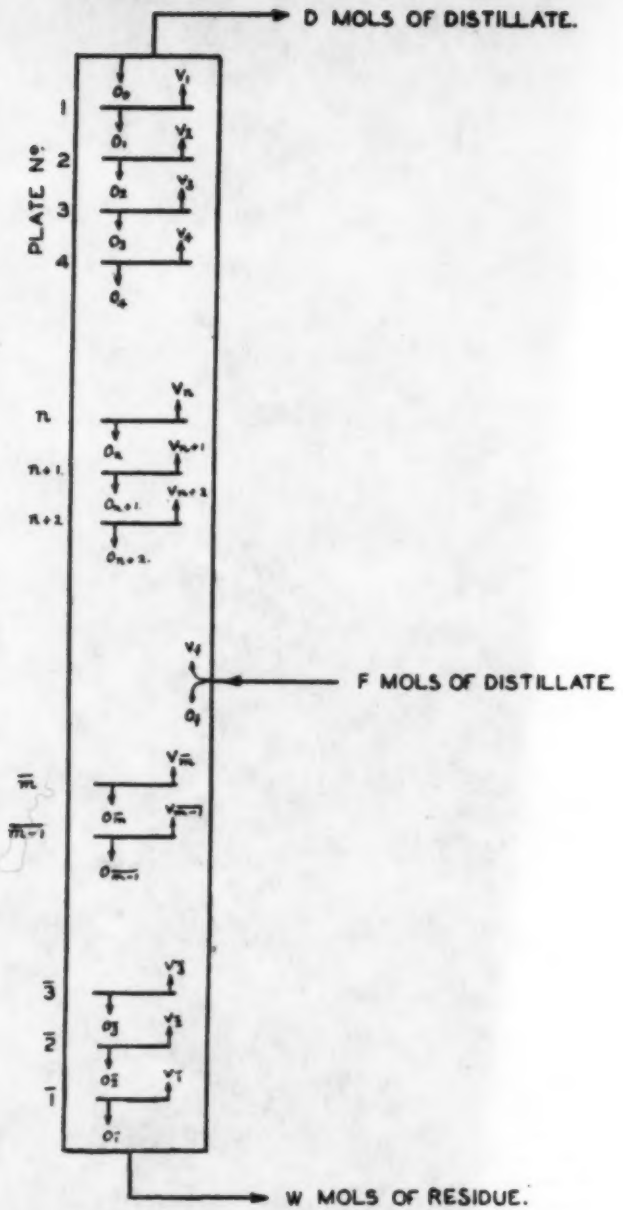


Fig. 1.

[To face p. 319.

UNIV. OF MICH.

calculation can then be made to obtain the composition at other points in the tower, and the composition so calculated may then be used :—

(*a*) in analysis, to obtain a value for plate efficiency by comparing the calculated composition with that actually obtained from analysis of the products from the tower;

(*b*) in design, to correct the initial assumption, and so finally arrive at the true composition of the products;

(*c*) or to calculate the number of theoretical plates required to effect a given separation.

The second of these is obviously a difficult step, and the method of carrying it out will be discussed at length. In the meantime, the reader should not allow this impending difficulty to worry him until the principle of the tabular calculation has been grasped.

### Derivation of Equation for Rectifying Section.

The equation for the rectifying section is derived on the assumption that the vapour rising from each plate is in equilibrium with the liquid on it. For towers working at low pressures (atmospheric or below) this equilibrium can be calculated by Raoult's Law, and this is done in the derivation. For towers at higher pressures equilibrium constants calculated from thermodynamic consideration [7] must be used. Their introduction will not alter the argument, and the method in which they may be introduced will be dealt with. A further assumption, already discussed, is that the ratio of the vapour pressures of two components can be considered constant over the operating temperature range of the section of the tower under consideration.

The feed to the tower is supposed to consist of a number of individual components, *A*, *B*, *C*, etc. In the case of a feed to a stabilizer these would be the pure hydrocarbons : in the case of a continuous mixture they would be a number of cuts of narrow boiling range.

### Equation for Rectifying Column.

Consider a tower as shown in Fig. 1. Then, by a material balance over the whole section of the tower above any plate in the rectifying column—say, for example, plate $n + 1$—we have :—

$$V_{n+1} = O_n + D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Taking a balance of component *A* :—

$$V_{n+1} A_{n+1} = O_n a_n + DA_d \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If vapour and liquid are in equilibrium on plate $n + 1$, we have :—

$$a_{n+1} P^a_{n+1} = \pi A_{n+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Substituting in equation (2) for $V_{n+1}$ (from equation (1)) and $A_{n+1}$ (from equation (3)) :—

$$(O_n + D)a_{n+1} \frac{P^a_{n+1}}{\pi} = O_n a_n + DA_d \quad . \quad . \quad . \quad . \quad (4)$$

Similarly for component *B*

$$(O_n + D)b_{n+1} \frac{P^b_{n+1}}{\pi} = O_n b_n + DB_d \quad . \quad . \quad . \quad . \quad (5)$$

Dividing (5) by (4) and rearranging:

$$\frac{a_{n+1}}{b_{n+1}} = \frac{a_n + \frac{D}{O_n} A_d}{b_n + \frac{D}{O_n} B_d} \times \frac{P^b_{n+1}}{P^a_{n+1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We shall now choose one of the components, which we shall call component $K$, as a reference component, so called because we shall refer the quantities of all other components to the quantity of $K$, by means of equations of the type of (6). This equation, with component $K$ in place of $B$, may be written:—

$$\frac{a_{n+1}}{k_{n+1}} = \frac{a_n + \frac{D}{O_n} A_d}{k_n + \frac{D}{O_n} K_d} \times \frac{P^k_{n+1}}{P^a_{n+1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

with similar equations for all the other components in which $B$, $C$, etc. are substituted for $A$.

Also let

$$\frac{P^a_{n+1}}{P^k_{n+1}} = \alpha_a,$$

where $\alpha_a$ is the volatility ratio of these two components, and may be taken as constant over the section of the tower. Values of $\alpha_a$, $\alpha_b$, etc. can be obtained from a vapour-pressure chart by writing down the vapour pressures of all components at the mean temperature of the section of the tower and dividing each vapour pressure by that of the reference component.* Then equation (7) becomes:—

$$\frac{a_{n+1}}{k_{n+1}} = \frac{a_n + \frac{D}{O_n} A_d}{k_n + \frac{D}{O_n} K_d} \times \frac{1}{\alpha_a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

or

$$a_{n+1} = \frac{k_{n+1}}{k_n + \frac{D}{O_n} K_d} \left( \frac{1}{\alpha_a} \left( a_n + \frac{D}{O_n} A_d \right) \right) \quad . \quad . \quad . \quad . \quad (8)$$

Putting

$$a^*_{n+1} = \frac{1}{\alpha_a} \left( a_n + \frac{D}{O_n} A_d \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$b^*_{n+1} = \frac{1}{\alpha_b} \left( b_n + \frac{D}{O_n} B_d \right) \text{ etc.}$$

we get

$$a_{n+1} = \frac{k_{n+1}}{k_n + \frac{D}{O_n} K_d} (a^*_{n+1}) \text{ etc.} \quad . \quad . \quad . \quad (10)$$

* In the case of towers working under high pressure, the value of the equilibrium constants (7) should be used in place of vapour pressure in order to obtain relative volatilities.

The sum of the mol fractions of all the components in the liquid on plate $n+1$ will equal 1, *i.e.*

$$\Sigma a_{n+1} = 1 = \frac{k_{n+1}}{k_n + \frac{D}{O_n} K_d} (a^*_{n+1} + b^*_{n+1} + c^*_{n+1} \ldots) \quad . \quad (11)$$

Therefore

$$\frac{k_{n+1}}{k_n + \frac{D}{O_n} K_d} = \frac{1}{\Sigma a^*_{n+1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Substituting this in equation (10) we get :—

$$a_{n+1} = \frac{a^*_{n+1}}{\Sigma a^*_{n+1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$b_{n+1} = \frac{b^*_{n+1}}{\Sigma a^*_{n+1}} \text{ etc.}$$

Equations (9) and (13) are the working equations for the rectifying section.

### Tabular Calculation For Rectifying Section.

Our next concern is to develop a convenient method of using these equations, and we will consider making the stepwise calculation from the top plate of a tower in which reflux is being returned which is of the same composition as the distillate (*i.e.* in which there is no fractionation in the condenser). We shall also take it that the distillate is in equilibrium with the liquid on the top tray. Then, starting with the mol fractions of various components $A, B, C \ldots K \ldots$, etc., in the distillate, which are equal to $A_d, B_d, C_d \ldots K_d \ldots$, etc., we calculate $a_1, b_1, c_1 \ldots k_1 \ldots$, etc., by the following equation, which expresses the fact that vapour and liquid are in equilibrium on the top plate :—

$$a_1 = \frac{\pi}{P_1^a} \times A_d = \frac{\pi}{P_1^k} \frac{A_d}{\alpha_a} (\text{since } P_1^a = \alpha_a P_1^k) \quad . \quad . \quad . \quad (14)$$

Now,

$$\Sigma a_1 = 1 = \frac{\pi}{P_1^k} \left[ \frac{A_d}{\alpha_a} \frac{B_d}{\alpha_b} \frac{C_d}{\alpha_c} \ldots + K_d \ldots \right] \quad . \quad . \quad . \quad (15)$$

$$\frac{\pi}{P_1^k} = \frac{1}{\Sigma \frac{A_d}{\alpha_a}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and substituting for $\frac{\pi}{P_1^k}$ in equation (14) we get :—

$$a_1 = \frac{A_d}{\alpha_a} \div \Sigma \frac{A_d}{\alpha_a}$$

or, if we write

$$a^*_1 = \frac{A_d}{\alpha_a}, \text{ etc.}$$

then

$$a_1 = a^*_1 / \Sigma a^*_1$$

The calculation is best made in a tabular form as follows :—

| Component. | Volatility Ratio. | Molecular Fraction in Distillate. | $a_1^\circ = \frac{A_d}{\alpha_a}$. | $a_1 = \frac{a_1^\circ}{\Sigma a_1^\circ}$. |
|---|---|---|---|---|
| $A$ | $\alpha_a$ | $A_d$ | $A_d/\alpha_a$ | $a_1$ |
| $B$ | $\alpha_b$ | $B_d$ | $B_d/\alpha_b$ | $b_1$ |
| $C$ | $\alpha_c$ | $C_d$ | $C_d/\alpha_c$ | $c_1$ |
| . | . | . | . | . |
| . | . | . | . | . |
| . | . | . | . | . |
| $K$ | 1·0 | $K_d$ | $K_d$ | $k_1$ |
| . | . | . | . | . |
| . | . | . | . | . |
| Sum | | 1·0 | $\Sigma a_1^\circ$ | 1·0 |

We next have to calculate the composition of the liquid on the second tray, this being the first of the series of steps in the stepwise calculation. Having calculated $a_1$, $b_1$, . . . as above we obtain $a_2$, $b_2$ . . . by means of the equations (9) and (13)

$$a_2^\circ = \frac{1}{\alpha_a}\left(a_1 + \frac{D}{O_1} A_d\right)$$

$$a_2 = \frac{a_2^\circ}{\Sigma a_2^\circ}$$

The value of $\frac{D}{O_1}$, which is the reciprocal of the molecular reflux ratio, is obtained from a heat balance on the column, or else a value for the reflux ratio is assumed and the necessary heat supply to the column is calculated later by heat balance.

The calculation is again made in tabular form, and since we require values of $A_d$, $B_d$, etc., $\alpha_a$, $\alpha_b$, etc., and $a_1$, $b_1$, etc., during the course of it, it is convenient to extend the table just given.

Having calculated $a_2$, $b_2$, etc., we can proceed in exactly the same way and with the same table to calculate the composition on the third tray $a_3$, $b_3$, etc.

The table as far as the third tray then becomes as printed on p. 323.

### Equation for Stripping Section and Tabular Calculation.

The equations applicable to a stripper corresponding to (9) and (13) are :—

$$A^\circ_{\overline{m+1}} = \alpha_a\left(A_{\overline{m}} + \frac{W}{V_{\overline{m}}} a_w\right) \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$A_{\overline{m+1}} = \frac{A^\circ_{\overline{m+1}}}{\Sigma A^\circ_{\overline{m+1}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

In these equations $\frac{W}{V_{\overline{m}}}$ is the reciprocal of the reboil ratio. It will be noted that whereas in the rectifying section we considered mol fractions in the

TABLE I.

*Tabular Calculation of Composition down a Rectifying Column.*

| | From V.-P. Chart. | | (3) ÷ (2). | (4) ÷ $\Sigma a_1^\circ$. | $\frac{D}{O_1} \times (3)$. | (5) + (6). | (7) ÷ (2). | (8) ÷ $\Sigma a_2^\circ$. | $\frac{D}{O_2} \times (3)$. | (9)+(10). | (11) ÷ (2). | (12) ÷ $\Sigma a_3^\circ$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (1). | (2). | (3). | (4). | (5). | (6). | (7). | (8). | (9). | (10). | (11). | (12). | (13). |
| Component. | Volatility ratio. | Molecular fraction in distillate. | Molecular proportions on plate 1. | Molecular fraction on plate 1. | | | Molecular proportion on plate 2. | Molecular fraction on plate 2. | | | Molecular proportion on plate 3. | Molecular fraction on plate 3. |
| | $\alpha_a = P^a/P^k$ | | $a_1^\circ = \frac{A_d}{\alpha_a}$ | $\frac{a_1^\circ}{\Sigma a_1^\circ} = a_1$ | $\frac{D}{O_1} \times A_d$ | $\frac{a_1}{O_1} \times A_d$ | $a_2^\circ = \frac{a_1 + \frac{D}{O_1} \times A_d}{\alpha_a}$ | $\frac{a_2^\circ}{\Sigma a_2^\circ} = a_2$ | $\frac{D}{O_2} \times A_d$ | $\frac{a_2}{O_2} \times A_d$ | $a_3^\circ = \frac{a_2 + \frac{D}{O_2} \times A_d}{\alpha_a}$ | $\frac{a_3^\circ}{\Sigma a_3^\circ} = a_3$ |
| A | $\alpha_a$ | $A_d$ | $a_1^\circ$ | $a_1$ | | | $a_2^\circ$ | $a_2$ | | | $a_3^\circ$ | $a_3$ |
| B | $\alpha_b$ | $B_d$ | $b_1^\circ$ | $b_1$ | | | $b_2^\circ$ | $b_2$ | | | $b_3^\circ$ | $b_3$ |
| C | $\alpha_c$ | $C_d$ | $c_1^\circ$ | $c_1$ | | | $c_2^\circ$ | $c_2$ | | | $c_3^\circ$ | $c_3$ |
| . . . | . . . | . . . | . . . | . . . | | | . . . | . . . | | | . . . | . . . |
| K | 1·0 | $K_d$ | $k_1^\circ$ | $k_1$ | | | $k_2^\circ$ | $k_2$ | | | $k_3^\circ$ | $k_3$ |
| . . . | . . . | . . . | . . . | . . . | | | . . . | . . . | | | . . . | . . . |
| N | $\alpha_n$ | $N_d$ | $n_1^\circ$ | $n_1$ | | | $n_2^\circ$ | $n_2$ | | | $n_3^\circ$ | $n_3$ |
| Sum | | 1·0 | $\Sigma a_1^\circ$ | 1·0 | | | $\Sigma a_2^\circ$ | 1·0 | | | $\Sigma a_3^\circ$ | 1·0 |

liquids on the plates, in the stripping section we consider mol fractions in the vapour. Further, the equations are arranged so that we work upwards from plate to plate, as opposed to working downwards in the rectifying section.

In making a calculation for a stripper, we start with the liquid leaving the reboiler, having composition $a_w$, $b_w$, etc., and start by calculating the vapour in equilibrium with it, which is taken to be the vapour rising into the first plate, and will have composition $A_{\bar{0}}$, $B_{\bar{0}}$, etc.
We have :—

$$A_{\bar{0}} = \frac{P^a}{\pi} a_w = \frac{P^b}{\pi} \alpha_a a_w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Now

$$\Sigma A_{\bar{0}} = 1 = \frac{P^b}{\pi} [\alpha_a a_w + \alpha_b b_w \ldots + k_w \ldots] \quad . \quad (20)$$

$$\frac{P^b}{\pi} = \frac{1}{\Sigma \alpha_a a_w} \text{ and } A_{\bar{0}} = \frac{a_w \alpha_a}{a_w \alpha_a}$$

Writing $A^*_{\bar{0}} = a_w \alpha_a$ we get

$$A_{\bar{0}} = \frac{A^*_{\bar{0}}}{\Sigma A^*_{\bar{0}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

This calculation and the subsequent stepwise calculation can then be made in tabular form, in a similar manner to that for the rectifying column, as shown in Table II.

## PART II.—APPLICATION OF THE METHOD TO DESIGN.

### Introduction.

Tables I and II will serve as models for all stepwise calculations in rectifying or stripping sections. We have so far avoided any detailed consideration as to the actual method of approach which must be used when applying the tabular calculation in a practical case.

When designing a tower we can fix our attention on the separation between two adjacent cuts. Thus in a tower with no side streams the separation between distillate and residue is considered. In a tower with side streams we can consider the separation between the overhead distillate and the first tray cut, or between the first and second, or second and third tray cuts, or, lastly, between the bottom tray cut and the residue.

We may, of course, wish to know the separation obtained between all the products in the tower, and each pair can be treated as a separate problem, except in the case where products of very narrow boiling range are made with poor fractionation. But in many cases experience gives a satisfactory guide to the separation for most of the products, and question arises as to the separation between only two of them, and this separation can then be calculated as a problem by itself.

The calculation of the separation between the distillate and the first tray cut proceeds exactly as in Table I. We have as the starting point the composition of the distillate, which, when a tower is being designed, will have to be assumed. Since the composition of the feed will be known, it

TABLE II.

*Tabular Calculation of Composition up a Stripping Column.*

| | From V.-P. Chart. | | (3) × (2). | (4) ÷ $\Sigma A^{\bullet}_{0}$. | $W/V_0 \times (3)$. | (5) + (6). | (7) × (2). | (8) ÷ $\Sigma A_1^{\bullet}$. |
|---|---|---|---|---|---|---|---|---|
| (1). | (2). | (3). | (4). | (5). | (6). | (7). | (8). | (9). |
| Component. | Volatility Ratio. | Molecular fraction in residue. | Molecular proportions in vapour to plate I. | Molecular fraction in vapour to plate I. | | | Molecular proportions in vapour from plate I. | Molecular fraction in vapour from plate I. |
| | $a_n = P^n/P^{\bullet}$. | | $A_0^{\bullet} = a_n a_0$ | $A_0 = \frac{A_0^{\bullet}}{\Sigma A_0^{\bullet}}$ | $W/V_0 \times a_w$. | $A_0 + \frac{W}{V_0} a_w$ | $A_1^{\bullet} = \frac{W}{a_w\left(A_0 + \frac{W}{V_0} a_w\right)}$. | $A_1 = \frac{A_1^{\bullet}}{\Sigma A_1^{\bullet}}$ |
| $A$ | $a_a$ | $a_w$ | $A_0^{\bullet}$ | $A_0$ | | | $A_1^{\bullet}$ | $A_1$ |
| $B$ | $a_b$ | $b_w$ | $B_0^{\bullet}$ | $B_0$ | | | $B_1^{\bullet}$ | $B_1$ |
| $C$ | $a_c$ | $c_w$ | $C_0^{\bullet}$ | $C_0$ | | | $C_1^{\bullet}$ | $C_1$ |
| . . | . . | . . | . . | . . | | | . . | . . |
| $K$ | 1·0 | $k_w$ | $K_0^{\bullet}$ | $K_0$ | | | $K_1^{\bullet}$ | $K_1$ |
| . . | . . | . . | . . | . . | | | . . | . . |
| $N$ | $a_n$ | $n_w$ | $N_0^{\bullet}$ | $N_0$ | | | $N_1^{\bullet}$ | $N_1$ |
| Sum | | 1·0 | $\Sigma A_0^{\bullet}$ | 1·0 | | | $\Sigma A_1^{\bullet}$ | 1·0 |

is possible to obtain the composition of the first tray cut by difference, since of the components in the neighbourhood of the cut point, that which does not appear in the distillate must appear in the first tray cut. This will be the *assumed* composition for the first tray cut. Starting with the assumed values of $A_d$, $B_d$, etc., we work, as in Table I, through the requisite number of stages to bring us to the tray on which the tray cut is taken, and so obtain a *calculated* composition for the first tray cut. If our initial assumption for $A_d$, $B_d$, etc., is correct, the assumed and calculated compositions for the first tray cut will be identical; if incorrect, the divergence between the assumed and calculated compositions is used to correct the first assumption. The actual method of making this correction is illustrated in a worked example in Part III.

There is a difficulty which will arise in practical application which may be mentioned here. If the composition of the tray cut in the case just considered is to be calculated from the composition of the distillate, then the assumed composition of the distillate must have values for all components present in the first tray cut, including the very heaviest, which will, of course, be present in the distillate in very small quantities indeed—quantities so small that it would be extremely difficult to make any reasonably correct assumption for them. This can be overcome by "adding in" these components at appropriate points in the tabular calculation. The process of doing so is simple, but is most easily grasped from the practical example given in Part III, and fuller consideration will be left till then. It is explained in the footnote to Table VIII.

If we are interested in the separation between two tray cuts, an assumption is made for the composition of the top tray cut, and the assumed composition for the second tray cut obtained by difference from the composition of the feed as before. The composition of the liquid on the top tray of the section under consideration will be the same as that of the top tray cut, and since the column above this tray does not enter into the calculation, this may be called tray 1. We then have values for $a_1$, $b_1$, etc., from our assumption. Values for $A_d$, $B_d$, etc., must also be worked out and inserted in the table, and it is important to realize that, in calculating them, the distillate, as far as this section of the tower is concerned, consists of all material removed from the tower above this section, including the tray cut from the top of the section. We shall then have filled in columns (1), (2), (3) and (5) in Table I, and the stepwise calculation can be started at once, and continued for the requisite number of stages to give the calculated composition of the lower tray cut. The method of using this to correct the initial assumption, and the necessity and method of "adding in" components, will be exactly as in the case of separation between distillate and first tray cut.

In calculating the separation between overhead distillate and residue (no side streams being taken) an assumption is made for the composition of the distillate, and that of the residue is obtained by difference. The stepwise calculation in the rectifying section is then made by Table I for the necessary number of stages to give the composition of the liquid on the bottom tray of this section—that is, the liquid falling into the flash zone. By Table II we make a stepwise calculation, starting with the composition of the residue—which is, of course, the same as the liquid in the reboiler—

to give the composition of the vapour rising from the top tray of the stripping section into the flash zone.

The comparison between calculated and assumed values is then made by taking a material balance for the various components entering and leaving the flash zone. This is considered more fully in Part III.

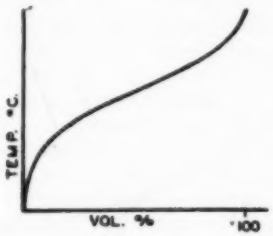


FIG. 2.

TRUE BOILING-POINT CURVES AND COMPOSITION CURVES.

Before proceeding to a more detailed consideration of the method of calculation, it is essential to consider the True Boiling-Point (T.B.P.) curves and composition curves for continuous mixtures, *i.e.*, those mixtures which contain so large a number of components boiling close together that the ordinary methods of analysis will not split the mixture up into its components. Such a mixture is best characterized by its true boiling-point curve usually drawn on a volume basis, as shown in Fig. 2. The first step when designing a column to fractionate the mixture is to draw the volume and molecular composition curves from the T.B.P. curve. It will be found that it is convenient, when drawing these curves, to consider the feed to

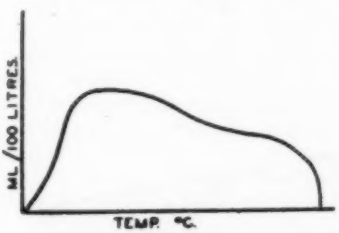


FIG. 3.

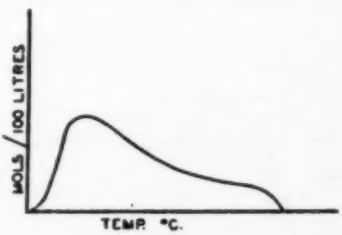


FIG. 4.

consist of a number of components each boiling 1° C. apart, or, as it is usually expressed, of a number of "1° C. components." It is also convenient to base these composition curves on 100 litres of feed, so that we finally arrive at curves showing ml. of 1° C. components in 100 litres of feed, and mols. of 1° C. components in 100 litres of feed, as shown in Figs. 3 and 4. The actual procedure for doing this is illustrated later.

(Note that these curves are not strictly composition curves, which would give ml. of 1° C. components in 100 ml. of feed, and mols. of 1° C. components in 100 mols. of feed, but the terms "volume composition

curve" and "molecular composition curve" will be used for these two curves for want of more acceptable ones.)

It is most necessary to grasp the significance and use of the composition curves. This discussion will be confined to the molecular composition curve, which is the most used, but applies equally to the volume composition

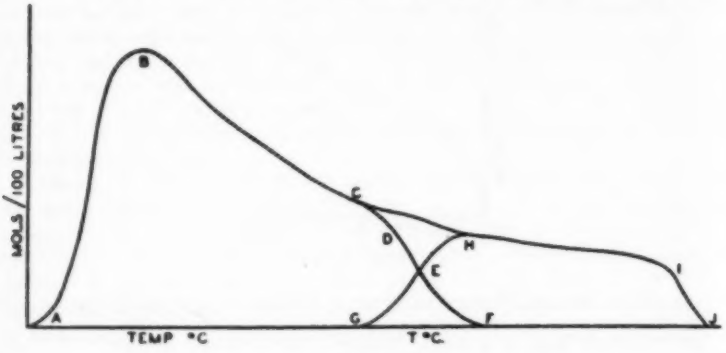


FIG. 5.

curve. Suppose, first, that we are going to take the feed and cut it at $t°$ C. with perfect fractionation. That is, all material boiling below $t°$ C. will appear in the distillate, and all boiling above in the residue. If we erect a vertical line at $t°$ C. in Fig. 5, the area to the left will be the composition curve of the distillate, and that to the right the composition curve of the residue. If the fractionation is not perfect, there will be some material boiling above $t°$ C. in the distillate, and some boiling below that temperature in the residue. The composition curve of the distillate will then be *A B C D*

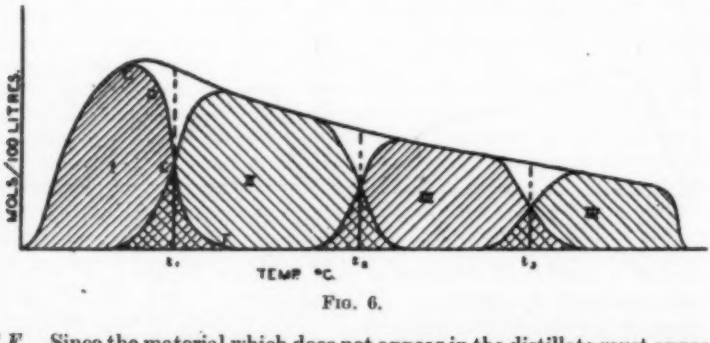


FIG. 6.

*E F*. Since the material which does not appear in the distillate must appear in the residue, the composition curve of the latter may at once be obtained by difference, and is *G E H I J*. These two curves cross at the point *E*, and therefore the component at this point is equally divided between distillate and residue. This component which is equally divided may be taken as that boiling at $t°$ C., the cut point.

If four products are produced from the feed—say a distillate overhead, two sidestreams and a residue—the cut points being $t_1$, $t_2$ and $t_3$ ° C., the resulting composition curves would be as shown in Fig. 6.

## Use of Composition Curves in Practice.

The use of the composition curves may be illustrated by considering the procedure involved when calculating the separation between overhead distillate and first tray cut.

It is assumed that the number of theoretical plates between the tower top and the first tray cut is known, and also the reflux ratio. The cut points $t_1$° C. between the distillate and the first tray cut, and $t_2$° C. between the first tray cut and the cut next below it are also known. The molecular composition curve is shown in Fig. 7. We can without loss of accuracy assume that the separation at $t_2$ is sharp, so that the composition curve of the tray cut can be terminated by a vertical line at this end. This is not

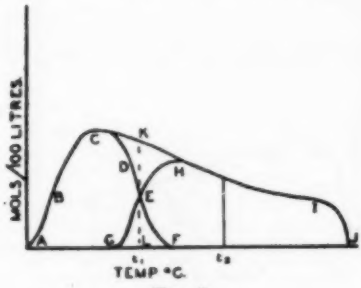


Fig. 7.

actually the case, but except when the tray cut is a very narrow one and is poorly fractionated, the distribution of the components in the region $t_2$° C. will not affect the distribution in the region $t_1$° C., which is that for which the calculation is being made, and the above procedure is justified. We can also assume that the component at the cut point $t_1$° C. will be equally distributed between the two cuts, so that the point $E$ is readily obtained. This assumption is not absolutely accurate. When the calculation has been completed, the result can be used to plot the volume composition curves for the two cuts, and from these the actual volume of distillate can be obtained. Reference to the T.B.P. curve will then show that the actual cut point is, say, $(t_1 + dt)$° C. The composition curves in the overlap region at $t_1$° C. can then be moved a small amount to right or left to allow for the difference between the cut point $t_1$° C. called for by the initial condition of the problem and that actually obtained in the calculation $(t_1 + dt)$° C.

The first assumption for the shape of the composition curve of the distillate must now be made—that is, for curve $A\ B\ C\ D\ E\ F$ (Fig. 7). There is no doubt as to the shape $A\ B\ C$, since in this region all material in the feed is in the distillate. Also point $E$ has already been fixed. There are various means by which the shape $D\ E\ F$ may be fixed. For instance, the

amount boiling above and below the cut point in the distillate and residue—that is, the amount of overlap and underlap—may be estimated by means of a set of overlap curves, and this fixes the areas *L E F* and *G E L*. If these areas are fixed, it is a simple matter to draw in the S-shaped curves *C D E F* and *G E H* to give curves of a reasonable shape with the correct areas *L E F* and *G E L*.

The initial assumption for the composition curves of the two cuts is made in this way; it will, of course, be far from correct, but even a very incorrect assumption will, it will be found, serve as an adequate starting point for the calculation. The calculation then proceeds as explained in the introduction to Part II.

Next consider the case of two unstripped tray cuts with cut points at $t_1$ (between overhead and first tray cut), $t_2$ (between the two tray cuts) and $t_3$ (between second tray cut and cut next below it in the column). The composition curves are shown in Fig. 8, sharp separation being assumed at $t_1$ and $t_3$, and the shape *C D E F* at $t_2$ being estimated by the overlap curves.

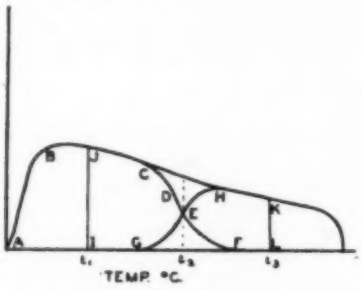


FIG. 8.

The composition curve for the *distillate* (which in this case includes the overhead and the first tray cut) is *A B C D E F*, and values of $A_d$, $B_d$, etc., are calculated from this. The composition curve for the first tray cut is *I J C D E F*, and values of $a_1$, $b_1$, etc., are calculated from it. The stepwise calculation is then made for $n$ plates, as in Table I. If a correct assumption for *C D E F* has been made, the calculated composition on plate $n$ (given by $a_n$, $b_n$, etc.) will be the same as the assumed composition given by the curve *G E H K L* (Fig. 8). The rules for correcting the initial assumption in order to make a more accurate second assumption are dealt with in Part III, in the practical example.

It will be clear from the two cases just considered as to what steps have to be taken in other cases, such as separation between overhead distillate and residue, tray cut and residue, etc., to make the necessary initial assumptions for the composition curves of the cuts the separation of which is to be calculated.

## PART III.—PRACTICAL CALCULATIONS.

### (*a*) CALCULATION OF SEPARATION BETWEEN TWO TRAY CUTS.

As an example, it is desired to calculate the separation between the 2nd and 3rd lub. cuts in a tower for which conditions and quantities of various

PLATE N°

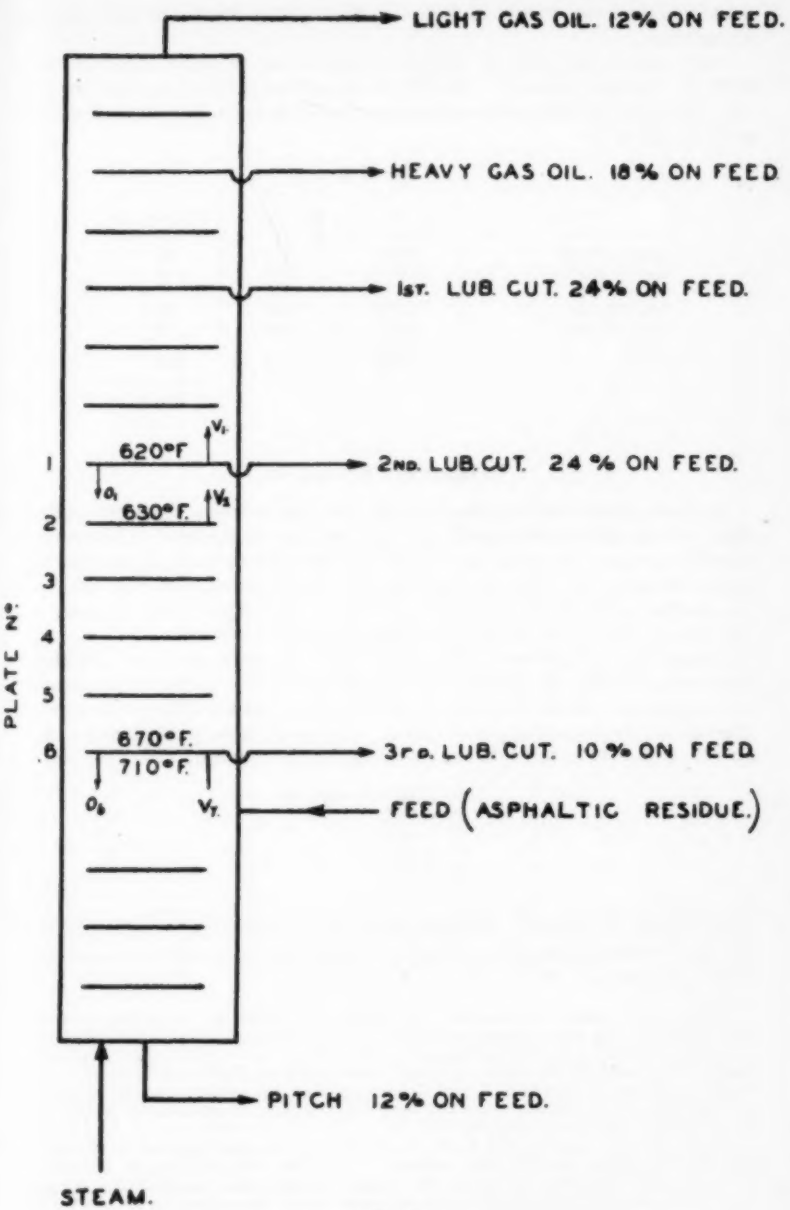
LIGHT GAS OIL. 12% ON FEED.
HEAVY GAS OIL. 18% ON FEED
1ST. LUB. CUT. 24% ON FEED.
620°F
2ND. LUB. CUT. 24% ON FEED.
630°F.
PLATE N°
1
2
3
4
5
6
670°F.
710°F.
3RD. LUB. CUT. 10% ON FEED.
FEED (ASPHALTIC RESIDUE.)
PITCH 12% ON FEED.
STEAM.

FIG. 9.

cuts produced are shown in Fig. 9. Five plates are to be used in the separation.

9800 barrels per day of asphaltic residue are charged together with 9000 lb. of steam per hour. The T.B.P.* curve of the feed is shown in Fig. 10. The weights of the cuts and the number of lb. mols. per hour are shown in Table III.†

TABLE III.

| Cut. | lb./hr. | mol. wt. | lb. mols./hr. |
|---|---|---|---|
| Light gas oil . . | 7,400 | 220 | 33·6 |
| Heavy gas oil . . | 11,200 | 260 | 43·1 |
| 1st lub. cut . . | 15,400 | 325 | 47·4 |
| 2nd lub. cut . . | 16,000 | 480 | 33·3 |
| 3rd lub. cut . . | 6,800 | 750 | 9·1 |
| Pitch . . . | 8,750 | — | — |
| Steam . . . | 9,000 | 18 | 500 |
| | | | 666·5 |

## OPERATING CONDITIONS.

The operation of the column is such that the overflow from the bottom tray into the flash zone is small, and may be taken to be zero. This requirement is necessary in order to keep down the temperatures in the pipe still outlet and stripper. The total pressure in the flash zone is 80 mm. Hg., and the partial pressure of oil vapour 20 mm. This figure will be taken as applying to the whole of the bottom section of the column.

From a heat balance we find that $O_1 = 89{\cdot}2$ lb. mols. per hour. Without very complicated calculations, it would be impossible to determine exactly the variation in the overflow from plate to plate, but we will assume a linear decrease as we pass from plates 1 to 6. The mols. flowing off plate 6 = 9·1, *i.e.* the mols. of the 3rd lub. cut produced by the column. We then have :

$O_1 = 89{\cdot}2$ lb. mols./hr.
$O_2 = 73{\cdot}2$
$O_3 = 57{\cdot}2$
$O_4 = 41{\cdot}2$
$O_5 = 25{\cdot}2$
$O_6 = 9{\cdot}1$

The mols. of distillate produced from the section under consideration is the sum of the two gas oils and the 1st and 2nd lub. cuts, and equals 157·4 lb. mols. per hour (*i.e.* 33·6 + 43·1 + 47·4 + 33·3).

* The T.B.P. curve is established by batch distillation up to a temperature of about 600° C., the high temperatures (450–600° C.) being estimated by distillation of a number of cuts of known percentage on the residue under 0·05 mm. Hg. pressure. The boiling points were converted by the chart given by Beale and Docksey.[1] The curve above 600° C. has been drawn to conform with the results of equilibrium flash experiments on the residue under 1–2 mm. Hg. pressure, in which up to 90 per cent. of the residue was flash vaporized.

† The densities used in the Table are obtained from experimental results giving the relation between density and boiling point. The molecular weights are derived from a curve based on the molecular weight–boiling point relationships for pure hydrocarbons and for petroleum fractions, particularly those given by Fensko.[4] This curve has been extrapolated to give the higher molecular weights.

Hence :—

$$D/O_1 = 1{\cdot}76$$
$$D/O_2 = 2{\cdot}14$$
$$D/O_3 = 2{\cdot}75$$
$$D/O_4 = 3{\cdot}82$$
$$D/O_5 = 6{\cdot}24$$

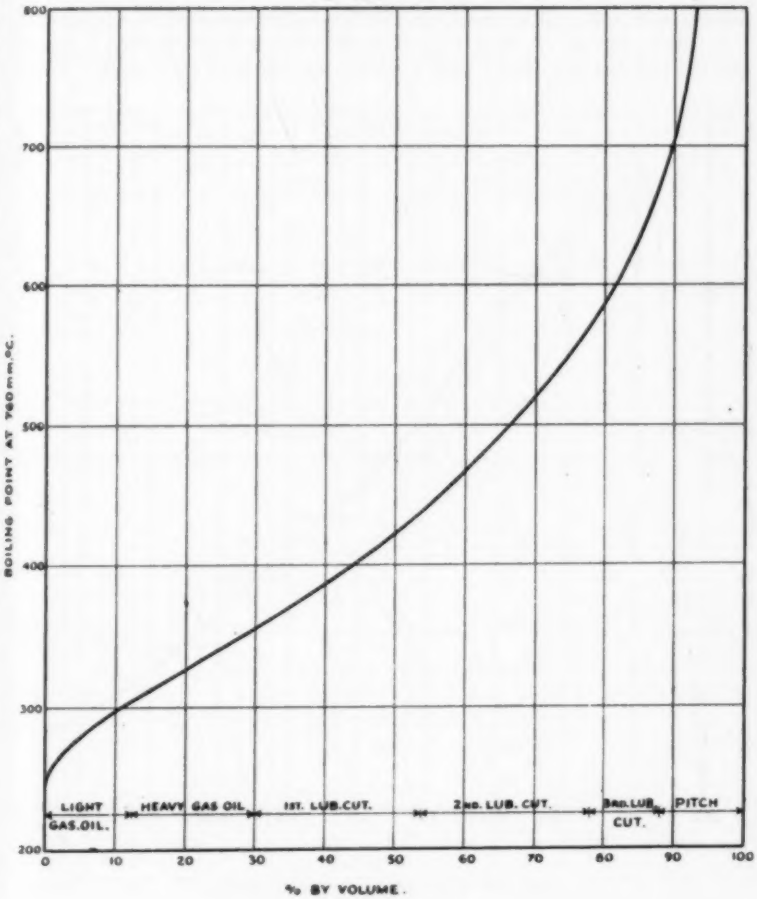


FIG. 10.

TRUE BOILING-POINT CURVE OF FEED.

## TRUE BOILING-POINT CURVE AND CUT POINTS.

The true boiling-point curve of the feed is shown in Fig. 10. The positions of the various cuts are marked, and the cut points are :—

| | |
|---|---|
| Light gas oil . . . . | 250–303° C. |
| Heavy gas oil . . . . | 303–354° C. |
| 1st lub. cut . . . . | 354–435° C. |
| 2nd lub. cut . . . . | 435–567° C. |
| 3rd lub. cut . . . . | 567–680° C. |

## Volume and Molecular Composition Curves.

The true boiling-point curve is next expressed as a volume composition curve. It is assumed that the residue consists of a number of pure compounds each boiling 1° C. apart, or, as it is usually expressed, of a number of 1° C. cuts. Curves are drawn showing the number of ml. of each 1° C. cut and the number of mols. of each 1° C. cut per 100 litres of residue. These

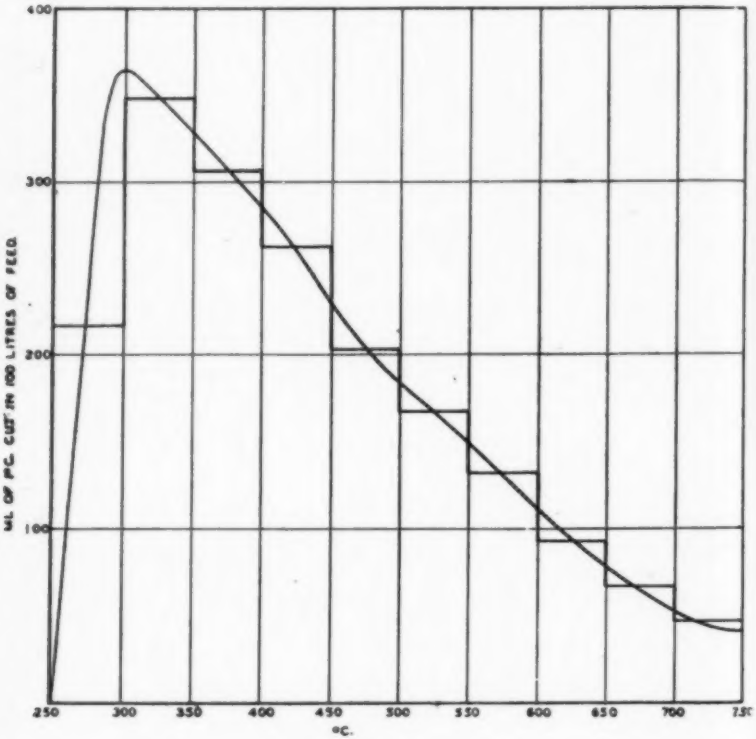


Fig. 11.

VOLUME COMPOSITION CURVE OF FEED.

are the volume and molecular composition curves, and are shown in Figs. 11 and 12. The method of deriving them from the T.B.P. curve is shown in the following table, where the T.B.P. curve is first split up into a number of 50° C. cuts, and the *average* number of ml. and mols. of the 1° C. components in each cut worked out. The figures obtained are plotted against the 50° C. temperature ranges as a series of steps, shown in Fig. 11, and the smooth curve drawn so as to give equal areas below the smooth curve and the stepped lines.

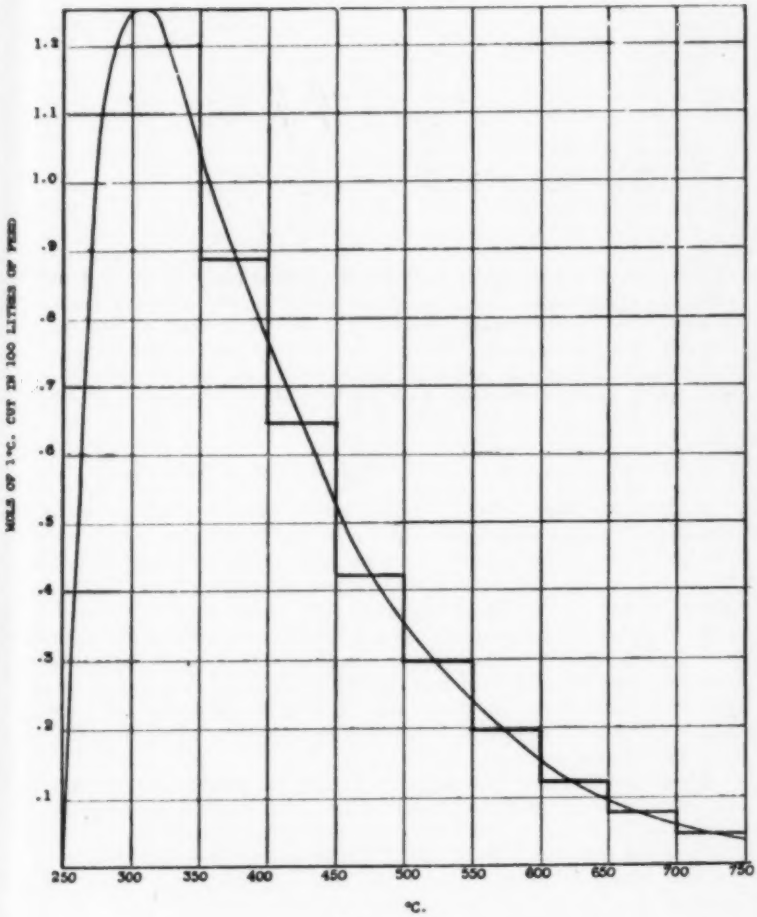


FIG. 12.

MOL. COMPOSITION CURVE OF FEED.

TABLE IV.

| Boiling Range of Cut. | Mean Temp., ° C. | Ml. of 50° C. Cut in 100 Litres of Residue. | Average ml. of 1° C. Cut. | Sp. Gr. at 60° F. | Mol. Wt. | Average Mols. of 1° C. Cut. |
|---|---|---|---|---|---|---|
| 250–300 | 275 | 10,800 | 216 | 0·840 | 205 | 0·886 |
| 300–350 | 325 | 17,400 | 348 | 0·864 | 251 | 1·200 |
| 350–400 | 375 | 15,300 | 306 | 0·888 | 307 | 0·885 |
| 400–450 | 425 | 13,100 | 252 | 0·909 | 370 | 0·644 |
| 450–500 | 475 | 10,100 | 202 | 0·930 | 447 | 0·420 |
| 500–550 | 525 | 8,300 | 166 | 0·948 | 535 | 0·294 |
| 550–600 | 575 | 5,400 | 128 | 0·966 | 640 | 0·193 |
| 600–650 | 625 | 4,600 | 92 | 0·983 | 760 | 0·119 |
| 650–700 | 675 | 3,300 | 66 | 1·00 | 885 | 0·075 |
| 700–750 | 725 | 2,200 | 44 | 1·016 | 1030 | 0·043 |
| 750–800 | 775 | 1,900 | 38 | 1·032 | 1210 | 0·033 |

The portion of Fig. 12 which covers the boiling range of the 2nd and 3rd lub. cuts is reproduced on a larger scale in Fig. 13. The cut points are indicated by vertical straight lines. The cut point between the 2nd and 3rd lub. cuts is given as 570° C. the correct value being 567° C. This small adjustment is made in order to give extra convenience in making the calculation, and the effect due to it can be corrected for afterwards.

### FIRST ASSUMPTION FOR COMPOSITION OF PRODUCTS.

If the cuts were perfectly fractionated, the compositions would be represented by the areas under the curves in Fig. 13 between the vertical straight lines. In practice there is some material in the 2nd lub. cut boiling above 570° C., and the mols. of the components boiling below (but close to) 570° C. are reduced, and the actual shape of the composition curve for the 2nd lub. cut will be approximately as shown by the curved line. Since the mols. of any component in the cut point region which do not appear in the 2nd lub. cut must appear in the 3rd lub. cut, the composition curve for the latter can be obtained at once by difference. It may be taken that the component at the cut point is equally split between the two cuts, which fixes the point at which the curves cross.

The actual curved shape adopted in Fig. 13 was determined by estimating the overlap to be expected by means of a set of overlap curves of the type suggested by Meyer.[6] The expected overlap plus underlap can be expressed as an area, shown in Fig. 13 as a triangle, and the S-shaped curves in the overlap region are drawn so that the area of overlap and underlap is the same as that shown by the triangle.

The composition curve of the 2nd lub. cut will also have a similar curved shape at the 435° C. region, and the same applies to the 3rd lub. cut in the 680° C. region. However, the shape of the curves for the two cuts at the extreme ends will not affect the separation between them, and it is far simpler to assume that at these ends they are perfectly fractionated.

It is obviously not necessary, when checking the correctness of the assumed separation in Fig. 13, to consider cuts of such close boiling range as 1° C. Cuts of boiling range 20° C. will be sufficiently close, and these

may be taken as having boiling ranges of 440–460° C., 460–480° C., etc. Each cut can then be characterized by its mid point, the two just mentioned being the 450° and 470° C. cuts. The number of mols. in each cut may be read from Figs. 12 or 13 by taking the ordinate at the mean temperature (*i.e.* at 450, 470, 490° C., etc.) and multiplying by 20. Thus the number of mols. of the 470 cut is $0{\cdot}437 \times 20 = 8{\cdot}74$.

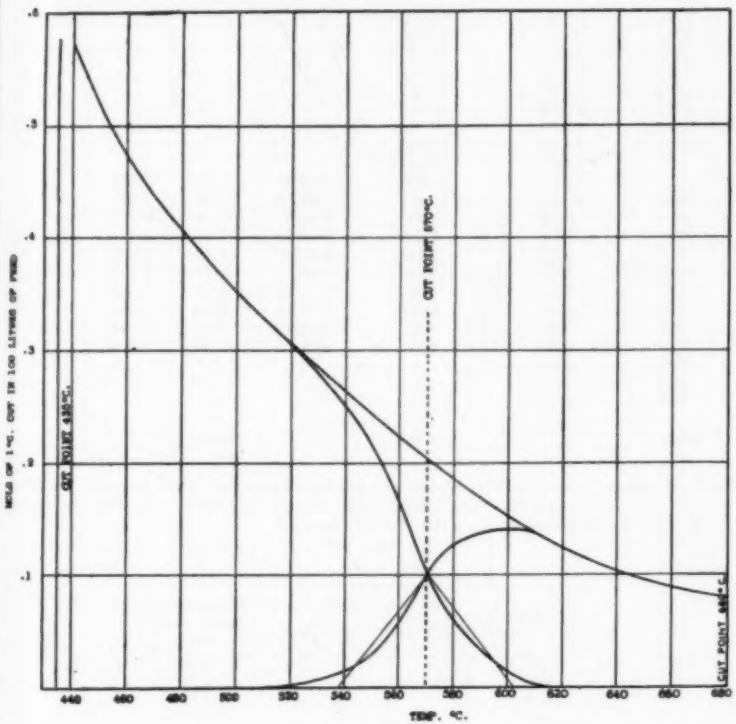


FIG. 13.

FIRST ASSUMPTION FOR COMPOSITION CURVES OF SECOND AND THIRD LUB. CUTS.

Table V gives the number of mols. of the 20° C. cuts in the feed, in the distillate, in the 2nd lub. cut and in the 3rd lub. cut, based on the assumed separation shown in Fig. 13.

The result of making the stepwise calculation for five plates using the values of $A_4$, etc., and $a_1$, etc., given in Table V is shown below. In order to compare the calculated and assumed values for the mols. in the 3rd lub. cut, the calculated values of $a_8$, etc., have been multiplied by a factor which makes the mols. of the 570° C. component equal to 2·03. This is done because by the initial assumption this value must be correct, and in a fresh assumption it will not be necessary to change it.

TABLE V.

*First Assumption.*

| Mid Pt. of 20° C. Cut, ° C. | Mols. in 100 Litres of Feed. | Mols. in Distillate, *i.e.* Gas Oils, and 1st and 2nd Lub. Cuts. | $A_4$, etc. | Mols. in 2nd Lub. Cut. | $a_1$, etc. | Mols. in 3rd Lub. Cut. |
|---|---|---|---|---|---|---|
| 255 | 1·90 | 1·90 | | | | |
| 270 | 16·00 | 16·00 | | | | |
| 290 | 24·20 | 24·20 | | | | |
| 310 | 25·00 | 25·00 | | | | |
| 330 | 23·40 | 23·40 | | | | |
| 350 | 21·00 | 21·00 | | | | |
| 370 | 18·50 | 18·50 | | | | |
| 390 | 16·40 | 16·40 | | | | |
| 410 | 14·40 | 14·40 | | | | |
| 430 | 12·44 | 12·44 | 0·0568 | 3·11* | 0·064 | |
| 450 | 10·40 | 10·40 | 0·0475 | 10·40 | 0·213 | |
| 470 | 8·74 | 8·74 | 0·0399 | 8·74 | 0·179 | |
| 490 | 7·54 | 7·54 | 0·0344 | 7·54 | 0·154 | |
| 510 | 6·56 | 6·56 | 0·0300 | 6·56 | 0·134 | |
| 530 | 5·68 | 5·50 | 0·0251 | 5·50 | 0·112 | 0·18 |
| 550 | 4·81 | 4·28 | 0·0196 | 4·28 | 0·088 | 0·53 |
| 570 | 4·06 | 2·03 | 0·0093 | 2·03 | 0·042 | 2·03 |
| 590 | 3·36 | 0·66 | 0·0030 | 0·66 | 0·013 | 2·70 |
| 610 | 2·80 | 0·04 | 0·0002 | 0·04 | 0·001 | 2·76 |
| 630 | 2·28 | — | — | — | — | 2·28 |
| 650 | 1·94 | — | — | — | — | 1·94 |
| 670 | 1·72 | — | — | — | — | 1·72 |
| Total | | 218·99 | | 48·86 | | |

* 3·11 mols. of this cut (= 12·44 ÷ 4) are included in the 2nd lub. cut, since the cut point is 435° C. and the boiling range in question is 420–440° C., so that one quarter of it may be considered to be in the 2nd lub. cut.

| Component. | Assumed Mols. in 3rd Lub. Cut. | Calculated Mols. in 3rd Lub. Cut. |
|---|---|---|
| 430 | — | 0·09 |
| 450 | — | 0·13 |
| 470 | — | 0·19 |
| 490 | — | 0·27 |
| 510 | — | 0·40 |
| 530 | 0·18 | 0·62 |
| 550 | 0·53 | 1·05 |
| 570 | 2·03 | 2·03 |
| 590 | 2·70 | 6·35 |
| 610 | 2·76 | 9·94 |
| 630 | 2·28 | 8·23 |
| 650 | 1·94 | 6·90 * |
| 670 | 1·72 | 6·11 |

These figures are plotted in Fig. 14.

* The values for the 630, 650 and 670° C. components are obtained by the process of "adding in." For a full description of the method see footnote to Table VIII. The process is such that the mol. fractions of the 610, 630, 650 and 670° C. components are relatively correct with each other in the 3rd lub. cut. Use is made of this fact in making the adjustment for the second assumption.

### Method of Adjusting Initial Assumption.

The next step is to use the information plotted in Fig. 14 to make a fresh assumption which will be more nearly correct.

The method by which this is done rests on the following two observations :—

(1) The amounts of material boiling well below the cut point are affected greatly by the amount in the distillate, and this means that the amounts of these components in the 3rd lub. cut when correctly calculated

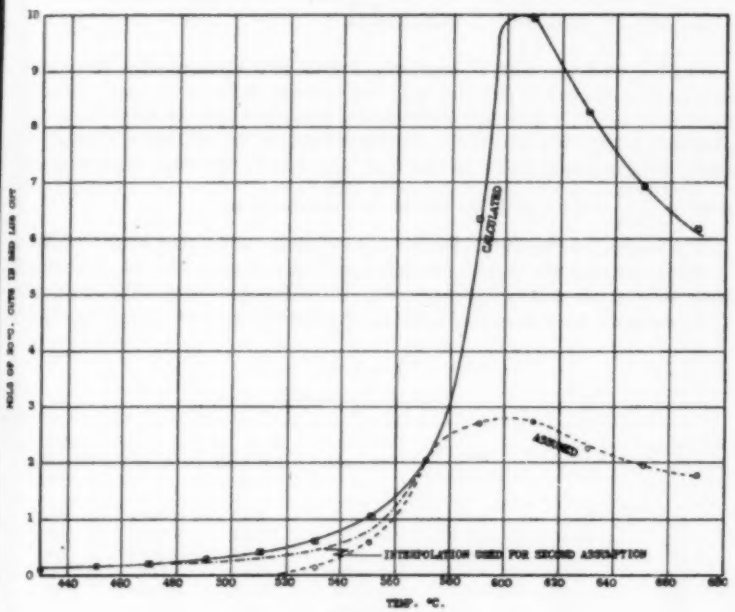


Fig. 14.

COMPARISON OF ASSUMED AND CALCULATED THIRD LUB. CUT COMPOSITIONS (FIRST ASSUMPTION).

will be close to those obtained on the first calculation. Consider the 470° C. component : we assumed there was none of this in the 3rd lub. cut and 8·74 mols. in the 2nd lub. cut. If we make a fresh assumption that there are 0·19 mol. in the 3rd lub. cut, and 8·55 mols. in the 2nd lub. cut, we shall disturb the figures in our preliminary calculation only slightly. This gives us a method of adjusting our original assumption at the lighter end.

(2) Consider the amounts of the 610, 630, 650 and 670 cuts : they are all in the correct proportions between themselves in the calculated composition for the 3rd lub. cut, for they were arranged to be so in the course of the calculation. Their absolute values are, however, all 3·58

times too great. Their calculated values depend on the initial assumption for the 610 component in the 2nd lub. cut, which we took as 0·04 mol. A more nearly correct value would be

$$\frac{0{\cdot}04}{3{\cdot}58} = 0{\cdot}0112 \text{ mol.}$$

(3) It should be noted that the assumed value for the 570 component is correct, since it was originally fixed that this component should be equally divided.

(4) We are now left with the problem of fixing suitable values for the 530, 550 and 590° C. components.

Dealing with the 590° C. component first, it is obvious that the amount originally assumed in the 2nd lub. cut was about twice as much as should have been taken. The calculated mols. in the 3rd lub. cut are 6·35, and the assumed 2·70. We will therefore correct the value of 0·66, the number of mols. of this component in the 2nd lub. cut in the first assumption, to $0{\cdot}66 \times \frac{2{\cdot}70}{6{\cdot}35} = 0{\cdot}28$ mol. for the second assumption.

The values for the 530 and 550 components are estimated by interpolating a curve between the calculated and assumed curves in Fig. 14, drawing the interpolated line somewhat nearer the calculated line for the 530 component. As a result, we obtain the following figures for the second assumption :—

TABLE VI.

*Second Assumption.*

| Mid Pt. of 20° C. Cut, ° C. | Mols. in Feed. | Mols. in Distillate. | $A_4$, etc. | Mols. in 2nd Lub. Cut. | $a_1$, etc. | Mols. in 3rd Lub. Cut. |
|---|---|---|---|---|---|---|
| 430 | 12·44 | 12·33 | 0·0568 | 3·02 | 0·0643 | 0·09 |
| 450 | 10·40 | 10·27 | 0·0472 | 10·27 | 0·2180 | 0·13 |
| 470 | 8·74 | 8·55 | 0·0394 | 8·55 | 0·1820 | 0·19 |
| 490 | 7·54 | 7·33 | 0·0338 | 7·33 | 0·1560 | 0·21 |
| 510 | 6·56 | 6·26 | 0·0289 | 6·26 | 0·1330 | 0·30 |
| 530 | 5·68 | 5·21 | 0·0240 | 5·21 | 0·1110 | 0·47 |
| 550 | 4·81 | 3·99 | 0·0184 | 3·99 | 0·0850 | 0·82 |
| 570 | 4·06 | 2·03 | 0·0093 | 2·03 | 0·0432 | 2·03 |
| 590 | 3·36 | 0·28 | 0·00129 | 0·28 | 0·00595 | 3·08 |
| 610 | 2·80 | 0·0112 | 0·0000516 | 0·0112 | 0·000238 | 2·79 |
| 630 | 2·28 | — | — | — | — | 2·28 |
| 650 | 1·94 | — | — | — | — | 1·94 |
| 670 | 1·72 | — | — | — | — | 1·72 |
| | | Total mols. in distillate = 217 | | 47·05 | | |

The results of the second assumption and the calculated number of mols. in the 3rd lub. cut are shown below. They are again expressed on the basis that the number of mols. of the 570° C. component is the same in both cases.

| Component. | Assumed Mols. in 3rd Lub. Cut. | Calculated Mols. in 3rd Lub. Cut. |
|---|---|---|
| 430 | 0·09 | 0·049 |
| 450 | 0·13 | 0·068 |
| 470 | 0·19 | 0·096 |
| 490 | 0·21 | 0·137 |
| 510 | 0·30 | 0·206 |
| 530 | 0·47 | 0·327 |
| 550 | 0·82 | 0·662 |
| 570 | 2·03 | 2·03 |
| 590 | 3·08 | 3·58 |
| 610 | 2·79 | 3·05 |
| 630 | 2·28 | 2·52 |
| 650 | 1·94 | 2·15 |
| 670 | 1·72 | 1·90 |

The result of the second calculation is shown in Fig. 15. The agreement below the cut point is now reasonably close. Following the rule given above, the calculated values for the mols. of components up to 510° C. will be taken for the third assumption, and interpolation made between the assumed

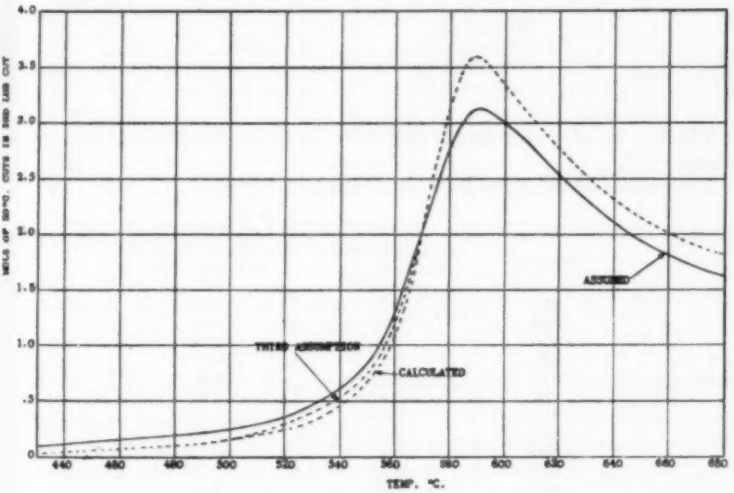


FIG. 15.

COMPARISON OF CALCULATED AND ASSUMED THIRD LUB. CUT COMPOSITIONS (SECOND ASSUMPTION).

and calculated values as shown for the 530 and 550° C. components. The 610° C. component was present in too large a quantity in the second assumption for the 2nd lub. cut, and should be reduced from 0·0112 to $0{\cdot}0112 \times \frac{2{\cdot}79}{3{\cdot}05} = 0{\cdot}0103$. The 590 component should be reduced from

0·28 to 0·28 $\times \frac{3{\cdot}08}{3{\cdot}58} = 0{\cdot}24$. We then obtain the following table for the third assumption.

TABLE VII.

*Third Assumption.*

| Mid Pt. of 20° C. Cut, ° C. | Mols. in Feed. | Mols. in Distillate. | $A_4$, etc. | Mols. in 2nd Lub. Cut. | $a_1$, etc. | Mols. in 3rd Lub. Cut. |
|---|---|---|---|---|---|---|
| 430 | 12·44 | 12·39 | 0·0520 | 3·06 | 0·0645 | 0·05 |
| 450 | 10·40 | 10·33 | 0·0476 | 10·33 | 0·2180 | 0·07 |
| 470 | 8·74 | 8·64 | 0·0398 | 8·64 | 0·1820 | 0·10 |
| 490 | 7·54 | 7·40 | 0·0341 | 7·40 | 0·1560 | 0·14 |
| 510 | 6·56 | 6·35 | 0·0292 | 6·35 | 0·1340 | 0·21 |
| 530 | 5·68 | 5·28 | 0·0243 | 5·28 | 0·1115 | 0·40 |
| 550 | 4·81 | 4·07 | 0·0187 | 4·07 | 0·0858 | 0·74 |
| 570 | 4·06 | 2·03 | 0·0093 | 2·03 | 0·0428 | 2·03 |
| 590 | 3·36 | 0·24 | 0·00110 | 0·24 | 0·00506 | 3·12 |
| 610 | 2·80 | 0·0103 | 0·0000475 | 0·0103 | 0·000217 | 2·79 |
| 630 | 2·28 | — | — | — | — | 2·28 |
| 650 | 1·94 | — | — | — | — | 1·94 |
| 670 | 1·72 | — | — | — | — | 1·72 |
| | | Total mols. in distillate = 217·1 | | 47·40 | | |

The full tabular calculation based on the above assumption is given in Table VIII.

The results of the third calculation are as follows :—

| Component. | Assumed Mols. in 3rd Lub. Cut. | Calculated Mols. in 3rd Lub. Cut. |
|---|---|---|
| 430 | 0·05 | 0·05 |
| 450 | 0·07 | 0·07 |
| 470 | 0·10 | 0·10 |
| 490 | 0·14 | 0·14 |
| 510 | 0·21 | 0·21 |
| 530 | 0·40 | 0·35 |
| 550 | 0·74 | 0·69 |
| 570 | 2·03 | 2·03 |
| 590 | 3·12 | 3·12 |
| 610 | 2·79 | 2·76 |
| 630 | 2·28 | 2·24 |
| 650 | 1·94 | 1·90 |
| 670 | 1·72 | 1·68 |

These figures are plotted in Fig. 16. The third assumption is obviously very close indeed, and can be taken without further alteration as the separation which will be obtained under the specified conditions. The figures in Fig. 16 converted back to mols. of 1° C. components (by dividing the figures for 20° C. components by 20) are shown in Fig. 17.

The corresponding curve showing millilitres of 1° C. cuts (based on 100

litres of feed) is shown in Fig. 18. From this curve the volume of the overlap can be obtained.

The cut point for the separation shown in Fig. 18 is 565° C., there being equal volumes boiling above and below this temperature in the 2nd and 3rd lub. cuts, respectively. The cut point called for by the initial conditions of the problem was 567° C. This would be obtained if the 572° C. instead of the 570° C. component were equally divided. The 592° C. component would then be split in the same ratio as the 590° C. component is in Fig. 18, *i.e.* the fraction in the 3rd lub. cut would be $\frac{108}{117{\cdot}5} = 0{\cdot}918$ and in the 2nd

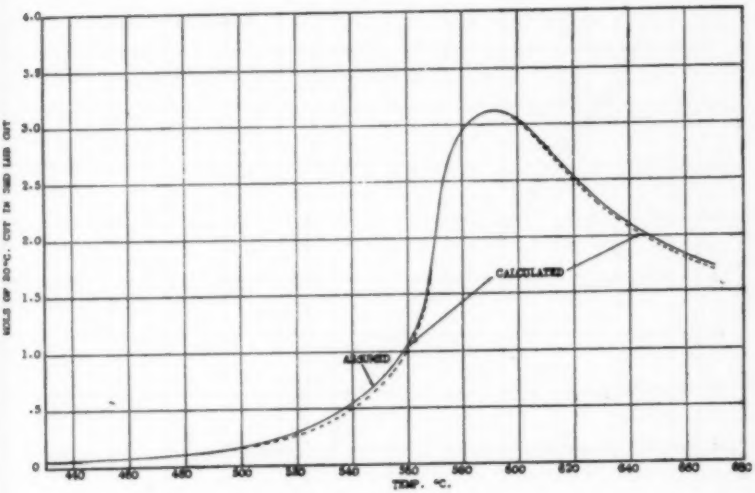


FIG. 16.

COMPARISON OF ASSUMED AND CALCULATED THIRD LUB. CUT COMPOSITIONS (THIRD ASSUMPTION).

lub. cut $\frac{9{\cdot}5}{117{\cdot}5} = 0{\cdot}082$. Since there are 114·5 ml. of the 592° C. component in the feed there will be $114{\cdot}5 \times 0{\cdot}918 = 105{\cdot}1$ ml. in the 3rd lub. cut and 9·4 ml. in the 2nd lub. cut when the adjustment has been made to give a cut point of 567° C. The other components can be adjusted in exactly the same way, and curves drawn through the points so obtained to give the composition curves of 2nd and 3rd lub. cuts having the corrected cut point.

### (*b*) Separation Between Overhead Distillate and Residue.

The method of procedure in a calculation involving both the rectifying and stripping section of the column has been briefly indicated, and must now be considered in more detail. Consider as a typical case the calculation of the separation of a given feed into overhead distillate and residue under known conditions of reflux and number of plates. The first opera-

tions are the same as those in the case just discussed—namely, to derive the mol. composition curve of the feed. The heat balance on the column, which is, of course, a necessary preliminary for all work of this kind, will have given the temperature of the flash zone, and an equilibrium flash calculation for the feed at this temperature must be made, to give the quantity and composition of the vapour and liquid obtained when the feed is flashed. These quantities will be required later. As in the previous case,

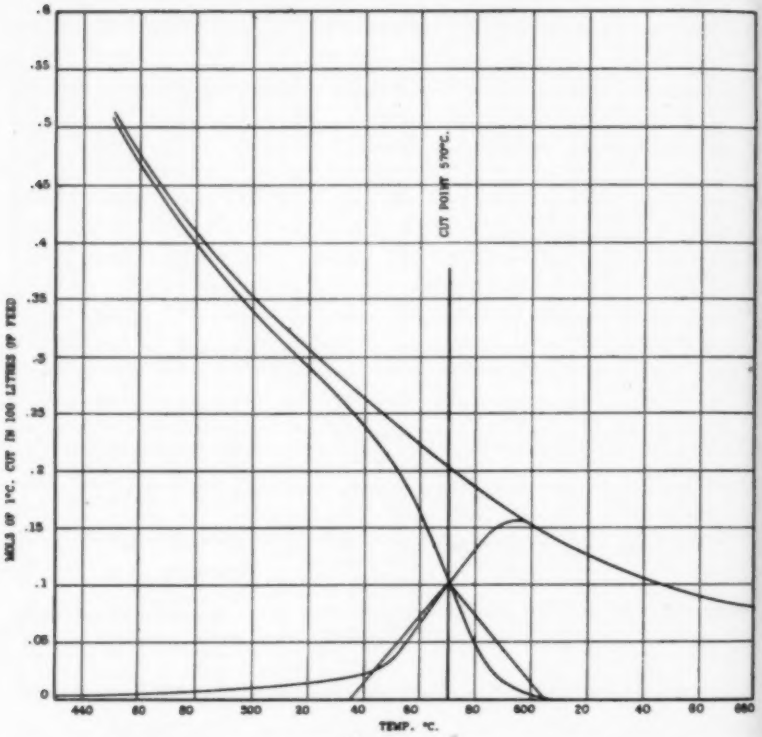


FIG. 17.

COMPOSITION CURVES OF SECOND AND THIRD LUB. CUTS (FINAL CALCULATION).

an assumption is made for the composition of distillate and residue. As already indicated, these assumed compositions are used to work out the composition of the liquid falling into the flash zone (by Table I) and the vapour rising into it (by Table II). Relative volatilities are taken at the mean temperature of each section. It will be obvious that the same difficulty will arise as in the case of the two tray cuts of assigning correct values for the small amounts of components boiling well above the cut point in the distillate and well below it in the residue, but which will rise to appreciable proportions when the flash zone is reached. This difficulty, it will be

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TABLE VIII.

| (1). | (2). | (3). | (5). | (6). | (7). | (8). | (9). | (10). | (11). | (12). | (13). | (14). | (15). | (16). | (17). |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\alpha$. | $A_d$. | $a_1$. | $1{\cdot}76\,A_d$. | $a_1 + 1{\cdot}76\,A_d$. | $a_2{}^*$. | $a_2$. | $2{\cdot}14\,A_d$. | $a_2 + 2{\cdot}14\,A_d$. | $a_3{}^*$. | $a_3$. | $2{\cdot}75\,A_d$. | $a_2 + 2{\cdot}75\,A_d$. | $a_4{}^*$. | $a_4$. |
| 430 | 41·0 | 0·0570 | 0·0645 | 0·100 | 0·164 | 0·0040 | 0·014 | 0·122 | 0·136 | 0·0033 | 0·005 | 0·157 | 0·162 | 0·004 | 0·004 |
| 450 | 24·2 | 0·0476 | 0·2180 | 0·084 | 0·302 | 0·0124 | 0·044 | 0·102 | 0·146 | 0·0060 | 0·010 | 0·131 | 0·141 | 0·006 | 0·006 |
| 470 | 14·75 | 0·0398 | 0·1820 | 0·070 | 0·252 | 0·0171 | 0·061 | 0·085 | 0·146 | 0·0099 | 0·016 | 0·109 | 0·125 | 0·008 | 0·008 |
| 490 | 8·97 | 0·0341 | 0·1560 | 0·060 | 0·216 | 0·0241 | 0·085 | 0·073 | 0·158 | 0·0176 | 0·028 | 0·094 | 0·122 | 0·014 | 0·014 |
| 510 | 5·38 | 0·0292 | 0·1340 | 0·051 | 0·185 | 0·0344 | 0·122 | 0·062 | 0·184 | 0·0342 | 0·055 | 0·080 | 0·135 | 0·025 | 0·025 |
| 530 | 3·10 | 0·0243 | 0·1115 | 0·043 | 0·155 | 0·0500 | 0·177 | 0·052 | 0·229 | 0·0738 | 0·118 | 0·067 | 0·185 | 0·060 | 0·060 |
| 550 | 1·765 | 0·0187 | 0·0858 | 0·033 | 0·119 | 0·0677 | 0·240 | 0·040 | 0·280 | 0·1585 | 0·252 | 0·051 | 0·303 | 0·172 | 0·172 |
| 570 | 1·00 | 0·0093 | 0·0428 | 0·016 | 0·059 | 0·0590 | 0·210 | 0·020 | 0·230 | 0·2300 | 0·366 | 0·026 | 0·392 | 0·392 | 0·392 |
| 590 | 0·563 | 0·00110 | 0·00506 | 0·0019 | 0·0070 | 0·0124 | 0·044 | 0·0024 | 0·0464 | 0·0825 | 0·132 | 0·003 | 0·135 | 0·240 | 0·240 |
| 610 | 0·302 | 0·0000475 | 0·000217 | 0·000083 | 0·00030 | 0·0010 | 0·0035 | 0·00010 | 0·0036 | 0·0119 | 0·019 | 0·0001 | 0·0191 | 0·0632 | 0·0632 |
| 630 | 0·164 | — | — | — | — | — | — | — | — | — | — | — | — | 0·0152 ‡ | 0·0152 |
| 650 | 0·090 | — | — | — | — | — | — | — | — | — | — | — | — | — | — |
| 670 | 0·048 | — | — | — | — | — | — | — | — | — | — | — | — | — | — |
| | | | | | | 0·2821 | 1·0005 | | | 0·6277 | 1·001 | | | 0·9994 | 0·9994 |

*Note* 1.—The headings of the columns in the above table are exactly the same as in Table I, and the columns are numbered identically in the two tables.

$b_4{}^*$, etc. (column (24)), by the factor $\frac{2{\cdot}03}{0{\cdot}352}$.

*Note* 2.‡—It will be observed that at this point a figure is inserted for the (630) component, and ‡'s mark similar insertions for the (650) and (670) compos

The ratio of the amounts of the (610), (630), (650) and (670) components on the bottom draw-off plate (plate 6) are accurately known, since so little o 2·28 : 1·94 : 1·72. Also it will be seen that in column (18) the figure for $D/O_4$ $(610)_4$ is negligible compared with $(610)_4$ (column (17)). This means that f though the operation were under total reflux, in which case we have :—

$$\frac{(610)_4}{(630)_4} = \left(\frac{a_{610}}{a_{630}}\right)^2 \times \frac{(610)_6}{(630)_6} \qquad \text{also} \quad \frac{(610)_4}{(630)_4} = \frac{(610)_4{}^*}{(630)_4{}^*}.$$

Substituting for $\frac{(610)_6}{(630)_4}$ in the first equation, and inserting values for all but $(630)_4{}^*$, which is unknown, we have $\frac{0{\cdot}0632}{(630)_4{}^*} = \left(\frac{0{\cdot}302}{0{\cdot}164}\right)^2 \times \frac{2{\cdot}79}{2{\cdot}28}$ $\therefore$

In a similar way :—$\frac{(610)_5{}^*}{(650)_5{}^*} = \frac{a_{610}}{a_{650}} \times \frac{(610)_6}{(650)_6}$. Inserting values $(650)_5{}^* = \frac{0{\cdot}210 \times 1{\cdot}94}{2{\cdot}79} \times \frac{0{\cdot}090}{0{\cdot}302} = 0{\cdot}0433$.

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| (16). | (17). | (18). | (19). | (20). | (21). | (22). | (23). | (24). | (25). | (26). |
|---|---|---|---|---|---|---|---|---|---|---|
| $a_4^*$. | $a_4$. | $3{\cdot}82\ A_4$. | $a_4 + 3{\cdot}82\ A_4$. | $a_5^*$. | $a_5$. | $6{\cdot}24\ A_4$. | $a_5 + 6{\cdot}24\ A_4$. | $a_6^*$. | $a_6$. | Mols. in 3rd Lub. Cut. |
| 0·004 | 0·004 | 0·218 | 0·222 | 0·005 | 0·003 | 0·356 | 0·359 | 0·0087 | 0·003 | 0·05 |
| 0·006 | 0·006 | 0·182 | 0·188 | 0·008 | 0·005 | 0·295 | 0·300 | 0·0124 | 0·005 | 0·07 |
| 0·008 | 0·008 | 0·152 | 0·160 | 0·011 | 0·008 | 0·248 | 0·256 | 0·0174 | 0·007 | 0·10 |
| 0·014 | 0·014 | 0·130 | 0·144 | 0·016 | 0·011 | 0·213 | 0·224 | 0·0250 | 0·009 | 0·14 |
| 0·025 | 0·025 | 0·111 | 0·136 | 0·025 | 0·017 | 0·182 | 0·199 | 0·0370 | 0·014 | 0·21 |
| 0·060 | 0·060 | 0·093 | 0·153 | 0·049 | 0·034 | 0·152 | 0·186 | 0·0600 | 0·023 | 0·35 |
| 0·172 | 0·172 | 0·072 | 0·244 | 0·138 | 0·094 | 0·117 | 0·211 | 0·1195 | 0·045 | 0·69 |
| 0·392 | 0·392 | 0·036 | 0·429 | 0·429 | 0·294 | 0·058 | 0·352 | 0·3520 | 0·132 | 2·03 |
| 0·240 | 0·240 | 0·004 | 0·245 | 0·435 | 0·297 | 0·007 | 0·304 | 0·5395 | 0·203 | 3·12 |
| 0·0632 | 0·0632 | 0·0002 | 0·0634 | 0·210 | 0·144 | 0·0003 | 0·1443 | 0·4780 | 0·180 | 2·76 |
| 0·0152 ‡ | 0·0152 | — | 0·0152 | 0·093 | 0·0636 | — | 0·0636 | 0·3880 | 0·146 | 2·24 |
| — | — | — | — | 0·0433 ‡ | 0·0296 | — | 0·0296 | 0·3290 | 0·124 | 1·90 |
| — | — | — | — | — | — | — | — | 0·2910 ‡ | 0·110 | 1·68 |
| 0·9994 | 0·9994 | | | 1·4623 | 1·0002 | | | 2·6575 | 1·001 | |

n the two tables. In column (26) the values of the mols. in the 3rd lub. cut are obtained by multiplying $a_4^*$,

and (670) components at later steps. The value to be inserted is obtained as follows :—

n, since so little of these components appears in the 2nd lub. cut. These ratios are (from Table VII) 2·79: This means that from plate 4 onwards the (610) component, and all those boiling higher, can be treated as

$$\frac{0)_4}{0)_4} = \frac{(610)_4^*}{(630)_4^*}.$$

$$\frac{2{\cdot}79}{2{\cdot}28} \qquad \therefore \quad (630)_4^* = \frac{0{\cdot}0632 \times 2{\cdot}28}{2{\cdot}79} \times \left(\frac{0{\cdot}164}{0{\cdot}302}\right)^3 = 0{\cdot}0152.$$

[*To face p.* 345.

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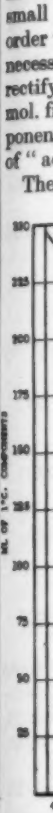


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remembered, was overcome in the previous case by the process of " adding in " for those components which were present in the top tray cut in such small proportions that they could not be estimated even roughly. In order to employ a similar process of " adding in " in the new case, it will be necessary to know the mol. fractions in the liquid on the bottom tray of the rectifying section of components boiling well above the cut point, and the mol. fractions in the vapour rising from the top tray of the stripper of components boiling well below the cut point. If these can be fixed, the process of " adding in " can be carried out in the manner used in Table VIII.

The mol. fractions of the components in question can be determined

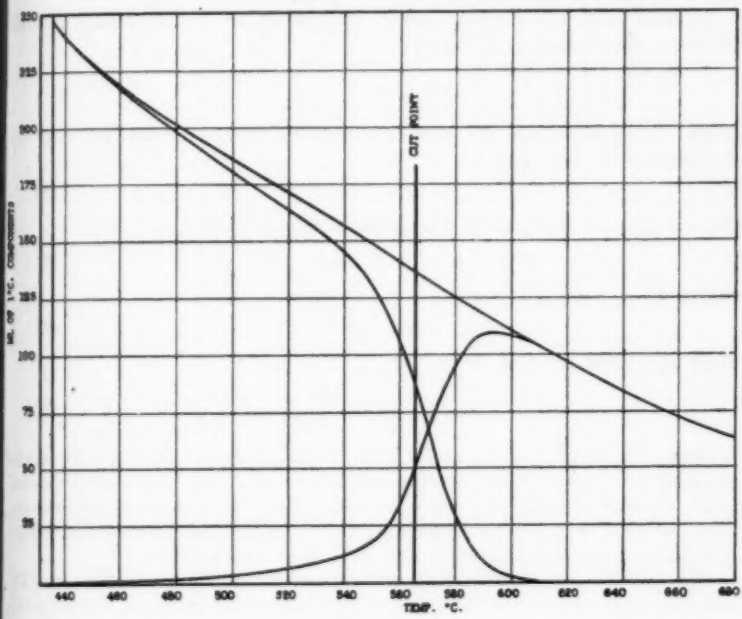


FIG. 18.

VOL. COMPOSITION CURVE OF SECOND AND THIRD LUB. CUTS.

roughly, but with sufficient accuracy for the purpose, by means of the following two equations, the first of which can be used to estimate mol. fractions of the lighter components (which appear only in the distillate) on the bottom plate of the rectifier, and the second for the mol. fractions of the heavier components in the vapour rising from the top plate of the stripper. The first of these equations is derived by Underwood,[11] and the second was derived in a similar manner and on similar assumptions.

$$a_n = \frac{A_d}{\{(R+1)(P_n^a/\pi) - R\}} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

(with similar equations for other light components),

where $R = O_n/D$ and $P_n^a$ = the vapour pressure of component $A$ at the temperature of plate $n$. This temperature can be estimated from the heat balance with sufficient accuracy.

$$Q_{\bar{m}} = \frac{Q_w}{\{(S+1)\,\pi\, P_{\bar{m}}^q - S\}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

(with similar equations for other heavy components),

where $S = \frac{V_{\bar{m}}}{W}$, and $P_{\bar{m}}^q$ = vapour pressure of component $Q$ at the temperature of plate $\bar{m}$. Component $Q$ has been chosen for this equation to indicate the fact that it applies for the heavier components.

In order to obtain $A_{\bar{m}}$, etc., and $Q_n$, etc., which are the quantities we wish to know, we proceed as follows :—

From Fig. 19 we have :—

$$O_n + O_f = O_{\overline{m+1}}$$

where $O_{\overline{m+1}}$ represents the mols. of liquid falling on to plate $\bar{m}$; and for component $A$, we have :—

$$O_n\, a_n + O_f\, a_f = O_{\overline{m+1}}\, a_{\overline{m+1}} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

By a balance of component $A$ over the stripping section :—

$$O_{\overline{m+1}}\, a_{\overline{m+1}} = V_{\bar{m}}\, A_{\bar{m}} + W a_w \quad . \quad . \quad . \quad . \quad . \quad (25)$$

and since $a_w$ is negligibly small :—

$$O_{\overline{m+1}}\, a_{\overline{m+1}} = V_{\bar{m}}\, A_{\bar{m}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

from equations (23) and (24) :—

$$A_{\bar{m}} = \frac{O_n}{V_{\bar{m}}} a_n + \frac{O_f}{V_{\bar{m}}} a_f \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Values of $O_n$ and $V_{\bar{m}}$ are obtained from the heat balance, and $O_f$ is obtained from an equilibrium flash calculation for the feed at the flash zone temperature. Values of $a_f$, $b_f$, etc., can also be obtained from the latter calculation, and the value of $a_n$ from equation (22). All the quantities on the right-hand side are therefore known, and $A_{\bar{m}}$ can be estimated.

The equation applicable to heavier components corresponding to (27) may be derived by a similar process, with the proviso that $Q_d$ is negligible, and is :—

$$q_n = \frac{V_f}{O_n} Q_f + \frac{V_{\bar{m}}}{O_n} Q_{\bar{m}}$$

Values of $V_{\bar{m}}$ and $O_n$ are obtained from the heat balance, $V_f$ and $Q_f$ from the equilibrium flash calculation on the feed and $Q_{\bar{m}}$ by equation (23). $q_n$ can thus be estimated.

In order to compare the calculated and assumed compositions obtained as the result of the stepwise calculation, a material balance is taken over the stripper as follows :—

If the bottom rectifying tray is $O_n$ and the top stripping tray $O_{\bar{m}}$, as in Fig. 19, we have by the stepwise calculation obtained values of

| | | |
|---|---|---|
| $a_n$, $b_n$ . . . . | etc. | (liquid falling into flash zone) |
| $A_{\bar{m}}$ $B_{\bar{m}}$ . . . . | etc. | (vapour rising into stripper) |

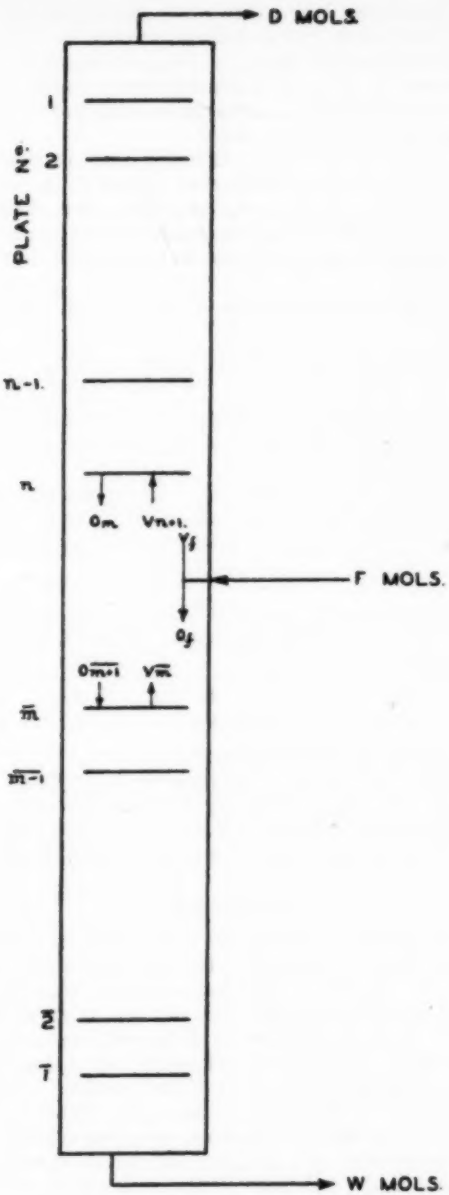


FIG. 19.

From the heat balance we have values of $O_n$ and $V_{\bar{m}}$, so that the mols. of each component falling from tray $n$ or rising from tray $\bar{m}$ can be immediately obtained, being, of course, $O_n a_n$, $O_n b_n$ . . ., etc., and $V_{\bar{m}} A_{\bar{m}}$, $V_{\bar{m}} B_{\bar{m}}$ . . ., etc. The heat balance will also give us the temperature to which the feed is heated on introduction into the flash zone, and the quantities of composition of the vapour and liquid derived from the feed

Let the mols. of vapour from the feed be $V_f$, and the composition $A_f$, $B_f$, etc., so that the mols. of each component will be $V_f A_f$, $V_f B_f$, etc. We can now derive the mols. of each component rising from the flash zone into tray $n$ in two ways the first being dependent on the stepwise calculation for the rectifying column, and the second on the stepwise calculation for the stripping column.

(1) From a material balance over the rectifying section, for component $A$ we have :—

Mols. of component $A$ leaving section $= DA_d + O_n a_n$
" " $B$ " " $= DB_d + O_n b_n$, etc.

The mols. of each component entering the section are the mols. rising from the flash zone, which to maintain a material balance must equal $(DA_d + O_n a_n)$, $(DB_d + O_n b_n)$, etc.

(2) The mols. rising from the flash zone can be obtained by adding the mols. vaporised from the feed to the mols. rising from the stripper. The mols. of the various components calculated in this way are :—

$$(V_{\bar{m}} A_{\bar{m}} + V_f A_f), (V_{\bar{m}} B_{\bar{m}} + V_f B_f), \text{ etc.}$$

If the initial assumption is correct, the mols. of the various components calculated in the two ways will be the same. If they are not equal, then a comparison between

$$(DA_d + O_n a_n) \text{ and } (V_{\bar{m}} A_{\bar{m}} + V_f A_f)$$
$$(DB_d + O_n b_n) \text{ and } (V_{\bar{m}} B_{\bar{m}} + V_f B_f), \text{ etc.,}$$

can be used to correct the initial assumption.

The comparison is best made by plotting $[O_n a_n + (DA_d - V_f A_f)]$, etc., against $V_{\bar{m}} A_{\bar{m}}$, etc., and using the graph so obtained to correct components below the cut point; and plotting $[V_{\bar{m}} A_{\bar{m}} - (DA_d - V_f A_f)]$, etc., against $O_n$, and using this graph to correct components above the cut point.

## Discussion.

It would not be possible in reasonable limits of space to discuss fully the many cases with which a method of fractionating tower design may be called to deal. Two important cases have been mentioned in the introduction, and must be discussed briefly. In the case in which the separation to be achieved forms the starting-point of the problem, and it is desired to calculate the number of plates, it is, of course, not necessary to make an initial assumption for the composition of the product. Consider the case in which the separation is between two tray cuts. Starting with the given composition of the top tray cut, we work down the column, and compare the calculated composition on each plate with the composition of the lower tray cut, selecting as the end plate of the section that on which the two compositions most nearly coincide. It is most unlikely that perfect

coincidence will be obtained, but there is no difficulty in selecting the correct plate. By means of a set of overlap curves the approximate number of plates can be estimated in advance, and, if this is done, the process of "adding in" can be used.

Another important application is in the analysis of fractionating towers, to determine plate efficiencies. The use of the Lewis and Wilde equation in this connection has already been mentioned. There is a disadvantage attached to its use in analysing the performance of towers distilling continuous mixtures. The whole accuracy of the estimation of efficiency depends on the accuracy of the analytical distillation of the products. The best results from this point of view would be obtained from a consideration of components close to the cut point. But for a component which is equally divided, as is the cut point component, no solution can be obtained, since it will be equally divided whatever the number of plates used. This applies in a lesser degree to the components close to the cut point, which are apt to give large errors in the estimation of plate efficiency, errors which are augmented if the intermediate plate temperatures have to be assumed.

On the other hand, if the stepwise method given here is used to make the estimation, attention is concentrated on the overlap and underlap as a whole. Indeed, the volume of the overlap and underlap only need be known, since it is easy to calculate the overlap and underlap which will be obtained under the known conditions of reflux ratio and temperature in the manner of the worked example given. The procedure, of course, gives overall plate efficiencies as opposed to individual plate efficiencies, but such figures are of the greatest use to the designer.

In conclusion, I wish to express my obligation to Mr. E. S. L. Beale for his very valuable suggestions and criticism, and to thank the Chairman of the Anglo-Iranian Oil Co., Ltd., for permission to publish this paper.

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# THE LUBRICATION OF JOURNAL BEARINGS IN OXIDIZING CONDITIONS.

By C. JAKEMAN and A. FOGG, M.Sc.


## SUMMARY.

(a) *Object of Investigation.*

The investigation was carried out to determine how much of the improvement obtained by prolonged running of a journal bearing in oxidizing conditions, as reported in a previous paper,* was attributable to oxidation of the lubricant, and whether blowing the lubricant with hot air before test would produce the same effect.

(b) *Range of Investigation.*

The experiments were made on N.P.L. journal friction machines with nickel chrome steel journals and bronze bushes. The lubricants were commercial varieties of mineral oils, all except one being types used for internal-combustion engine lubrication. Oxidizing conditions during running were obtained by means of hot air at 160° C. blown into the oil during circulation in the machine; a wash-leather filter was used in the oil-circulating system. In all cases the conditions of the tests were as follows: Load: 1000 lb./in.$^2$; speed: 1300 r.p.m.; diametral clearance between bush and journal: 0·008 inch.

(c) *Results.*

Starting with a new bush and running to seizure about every 6 or 7 hours, the seizing temperature of one of the oils increased from about 200° C. to about 300° C., and the minimum coefficient of friction decreased from 0·0008 to 0·0005$_5$ in a period of about 30 hours. A sample of the same oil, subjected to oxidizing conditions before running in the machine, gave similar results. When a sample of the new oil was run in one of the bushes which had already been used, the same values, seizing temperature 300° C. and minimum coefficient of friction 0·0005$_5$, were reached, after one or two seizures. Each of several other lubricants tested in a bush already "run-in" gave its optimum performance on the first run, and further blowing did not affect the results.

The improvement in seizing temperature and minimum friction was also obtained when fresh oil was fed to the bearing continuously, any possibility of cumulative oxidation being eliminated.

(d) *Conclusion.*

In the case of the oils examined, little, if any, of the improved performance is due to change in the lubricant, but to changes in the form of the bush and in the quality of the running surface.


## INTRODUCTION.

A PREVIOUS investigation† appeared to show that prolonged running of a journal bearing when the lubricant was subjected to blowing with hot air caused a fall in the minimum coefficient of friction and a rise in the seizing

* King and Jakeman, "Lubrication in Oxidizing Conditions," Aeronautical Research Committee, R. & M. No. 1517. See also R. O. King, "The Beneficial Effect of Oxidation on the Lubricating Properties of Oil," *Proc. Roy. Soc.*, A, 1933, **139**, 447–459, and R. O. King, "Oxidation Lubrication and the Blending of Mineral Oils to obtain Maximum Lubricating Value," *Journ. Inst. Pet. Tech.*, 1934, **20**, 97–114.

† King and Jakeman, "Lubrication in Oxidizing Conditions," Aeronautical Research Committee, R. & M. No. 1517.

temperature. The observations were in agreement with the general behaviour of oils tested before the investigation was commenced, and the improvement noted was attributed to a change in the lubricants. To explain the phenomena observed, King put forward a theory of oxidation lubrication which is fully described in the report of the above investigation.

The new series of tests was undertaken in conjunction with the Air Ministry Laboratory, in order to ascertain whether there was any explanation, other than oxidation of the oil, of the experimental results.

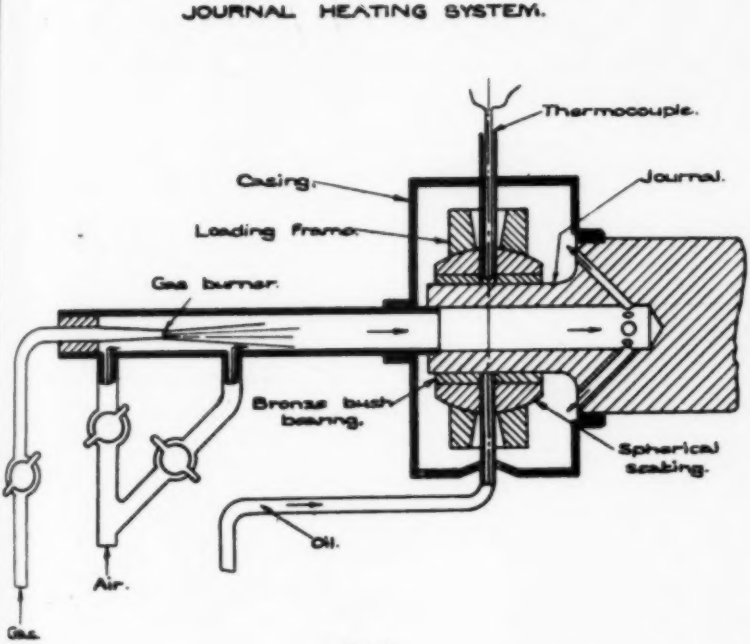



FIG. 1.

## DESCRIPTION OF JOURNAL FRICTION MACHINE.

The journal is 2 inches diameter by $3\frac{1}{2}$ inches long, formed on the end of a nickel chrome-steel shaft 4 inches diameter, which is mounted in two roller bearings and driven by a belt from a variable-speed electric motor. The bush is of special bronze (87·9 per cent. copper, 11·8 per cent. tin) $2\frac{1}{2}$ inches long, and is fitted into a steel shell which is accommodated in a cast-iron holder with spherical seating, as shown in Fig. 1. The loading system is shown diagrammatically in Fig. 2. A load is hung on the end of the lower lever and transmitted to the middle point of a short horizontal link, the ends of which are connected by vertical links to the bush-holder. The friction torque on the bush tends to rotate the bush-holder and to distort the loading-frame. This torque is balanced by a load applied to an extension of the short

horizontal link. In order to ensure that this link is horizontal, a tube with a lens focussed on a fiducial mark on the link extension is employed, and the friction balance weights are adjusted so that the fiducial mark coincides with a line on the lens.

### Heating Apparatus.

The temperature of the bearing is raised by means of the gas-burner shown in Fig. 1. The hot gases formed by combustion at the back end of the tube pass through the hollow journal and discharge through diagonal holes into the case surrounding the bearing. This has been found to give very uniform heating of the bush. The temperature is measured by a thermocouple placed in a hole drilled into the wall of the bush at the top to within about 0·02 inch of the running surface.

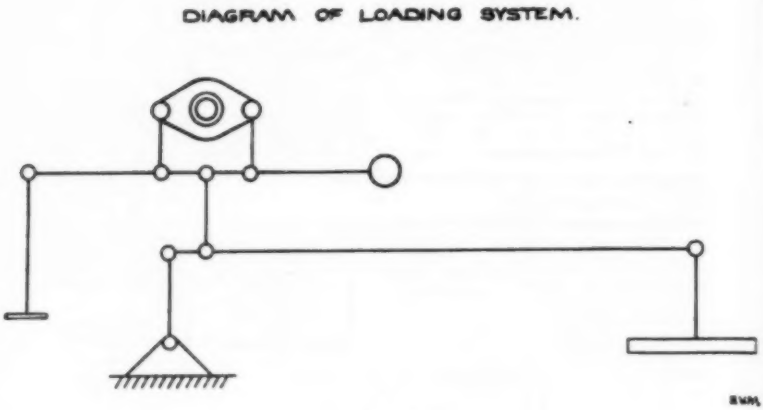



Fig. 2.

### Oil Feed.

The oil-circulating system is shown in Fig. 3. About two gallons of oil are placed in the sump, and the oil is fed to the lower (unloaded) side of the bush by means of a pump driven independently of the machine by a separate electric motor. After passing through the bearing, the oil is collected in a tray and returned to the sump through a wash-leather filter. This replaces the gauze filter used in the previous investigation, and is the only modification of the test conditions. Its effect is to remove many metallic and dust particles which would have passed a gauze filter. With this improvement the consistency of successive determinations of the seizing temperature is greater, and observations on one oil can be more closely repeated on different bushes.

The rate of oil-feed is to a certain extent limited by the capacity of the filter, which varies with the viscosity of the oil; in these tests the rate varied from 2 fluid oz. per minute when the oil was cold to about 8 fluid oz. per minute just before seizure.

### Blowing the Oil During a Test.

The oil was blown by air at a temperature of about 160° C. as it passed down the drain-pipe to the filter. The electric heater and the position of mixing with the oil are shown in Fig. 3. During those experiments when

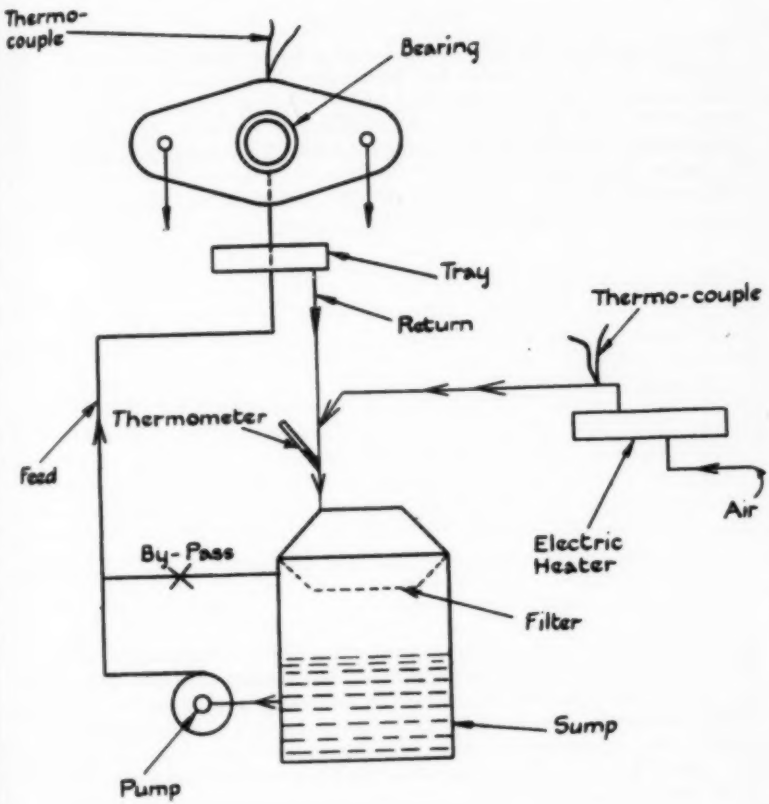



Diagram of lubricating system.

Fig. 3.

the oil was not blown, the air supply was shut off entirely in addition to switching off the heater.

### Blowing the Oil Before Test.

A special apparatus was used for blowing a sample of oil before test. A sample of oil (about 2 gallons) was placed in a vessel and circulated through a

pipe at a rate of 600 ml. per minute, the oil in the vessel being maintained at a temperature of 70° C. by means of immersion heaters. At one point of the circulating system the oil passed through a jet, at right angles to which was another jet passing air at a temperature of 165° C. and at a rate of 0·2 gm. per second. This treatment was continued for 24 hours.

## Method of Test.

The journal of the machine was polished to a fine finish to an accuracy of $\pm$ 0·00005 inch in circularity and parallelism. The bushes were finished to the same accuracy by boring in a lathe to as fine a finish as possible to within 0·001 inch of the required diameter, followed by polishing with "blue-back" emery papers to the required size, about 0·008 inch more than the journal diameter.

The tests were made at a load of 1000 lb./in.$^2$ of projected area, and at a

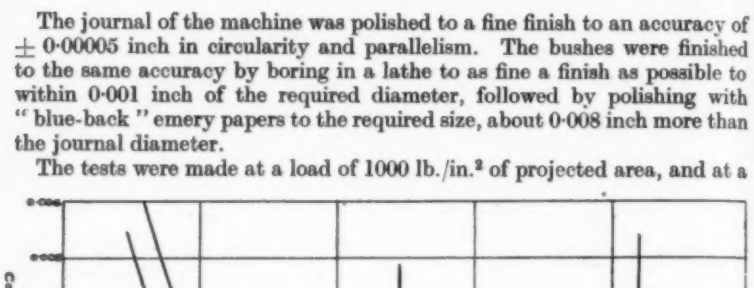



Fig. 4.

speed of 1300 r.p.m. (11·3 ft./sec.) the temperature was gradually raised to the temperature of minimum friction and maintained at this temperature for some hours. At the end of each day the temperature was raised until seizure occurred. The curve of coefficient of friction plotted against temperature was drawn for each test. The average time of running per day was about 7½ hours, of which time the first hour was required for heating up to the temperature of minimum friction and 1½ hours for the final heating up to seizure. During the remaining 5 hours the bearing was run at the temperature of minimum friction. On Saturdays the total time of running was about 3 hours.

An exception to this procedure was made in the final tests recorded, in which fresh oil was continuously supplied to the bearing. The intermediate stage in which the bearing was run at constant temperature was omitted in order to reduce the quantity of oil used.

## Interpretation of the Friction Temperature Curve.

The general forms of the friction temperature curve are shown in Fig. 4, where the coefficient of friction is plotted against the temperature of the

bush. Curve (*a*) is the type desirable, since there is a large minimum friction range of temperature or margin of safety before seizure. Curve (*b*) is a common form of curve obtained especially during the early stages of a test. The curves may be divided into three stages : (1), (2) and (3) as marked on curves (*a*) and (*b*).

*Stage* (1)

The coefficient of friction falls as the viscosity of the oil decreases with increase of temperature; this is the region of fluid film lubrication.

*Stage* (2)

During this stage the decrease in friction ceases, and it would appear that the effect of decrease in viscosity with increase of temperature has been compensated by the increase of viscosity due to the pressure in the oil film and/or by an increase of viscous friction due to an increase of eccentricity of the bearing.

*Stage* (3)

In the third stage the friction increases at a rapidly increasing rate as the temperature rises, the final part of the curve rising at right angles to the temperature axis. The value of $\mu$ rarely exceeds 0·01 before either the load is removed or the driving-belt slips off the pulleys. The temperature at which this occurs is recorded as the seizing temperature.

It is thought that the surfaces come so nearly together that the condition of boundary friction occurs on the high spots, fluid film lubrication being maintained over the remainder of the surface. A transition from fluid film lubrication to boundary conditions then takes place gradually over more of the surface, until the amount of boundary friction present causes the bush to seize on the journal, owing to the large amount of heat generated. It is possible that the bearing will run with boundary friction occurring on the high spots, provided that these areas are small compared with the total area of the surface and that fluid film lubrication exists over the remainder. Under this condition the heat generated would be rapidly dissipated by the oil flowing under hydrodynamic conditions through the remainder of the bearing. Thus suppose that the minimum coefficient of friction under fluid conditions is 0·0006, and the coefficient of friction under boundary conditions is 0·15, then contact with high spots extending to 1 per cent. of the surface would raise the observed coefficient of friction to 0·0021.

A change in the shape and the surface condition of the bush occurs with continued running in the region shown by the third stage of the friction temperature curve. Measurements of the profiles of radial sections of bushes have shown that with prolonged running and several seizures the effective radius of the crown of the bush decreases in many cases, to become closely equal to the radius of the journal. This is brought about by wear and/or by compression or plastic flow of the metal. The change in effective clearance thus produced alters the form of the friction-temperature curve.

The curve shown in Fig. 5 indicates a change in the shape of the crown and surface condition of the bush. In this experiment, using castor oil as the lubricant, the bearing appeared to be on the point of seizing at the stages shown by the peaks in the curve. On cooling the bearing, the observations

fell on a smooth curve as shown, while the range of low friction had been increased.

Tests have also been made by running a bearing for long periods at a temperature above that of minimum friction and below the temperature of seizure. The visual result was to polish the surface, and such an improvement might be expected to make it possible to run with a thinner oil film, and an increase in the temperature would follow before seizure occurred.

## Factors Affecting Determination of Seizure.

The factors which affect the accuracy of determination of seizure may be divided as follows :—

(*a*) If the knife edges of the testing-machine become worn, there is the possibility of unequal loading along the length of the bush in spite of the

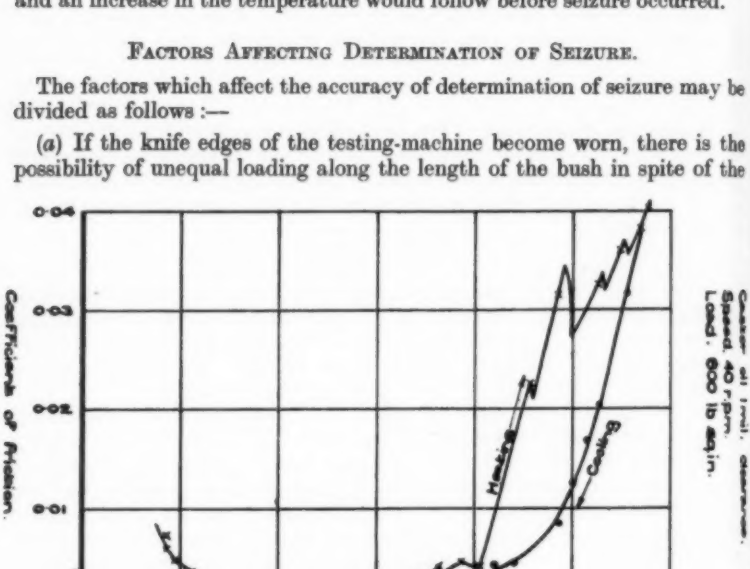



Fig. 5.

spherical seating, causing failure at the end under the greatest pressure. This can generally be detected by examination of the area of the bush which becomes marked through seizure.

(*b*) The accidental passing of a piece of hard grit through the bearing may cause scratches resulting in deterioration of the surface in process of alteration. This appears to be practically eliminated by the use of a wash-leather filter.

(*c*) The uniformity and surface finish of the bush initially are dependent on the skill of the mechanic. The compression of the metal in pressing the bush into the shell, the initial strains in the metal and the distortion by heat depend on the nature of the metal. The latter cannot be exactly controlled, and variations between different batches of castings may be expected.

(*d*) In the stage immediately preceding seizure, the oil film must be in an unstable condition, and an accidental oscillation of the friction arm of the machine while the balance weights are being changed may easily cause

premature failure. During the early stages of running the rate of heating between minimum friction and seizure is also important, for if at any of the peaks shown in Fig. 5 the rate of heating had been high, seizure would undoubtedly have occurred before recovery could take place.

## The Oils Examined.

Oil *A* was a proprietary summer-grade motor-car engine oil. The successive samples employed are denoted by *A*(1), *A*(2), etc., while *A*(0) denotes the sample of oil *A* subjected to oxidation conditions before test, as described previously.

Oil *B* was supplied by the Air Ministry Laboratory for these tests, and consisted of a blend of Pennsylvanian Bright Stock with Pennsylvanian distillates. Successive samples are denoted *B*(1), *B*(2), etc.

Oil *X* was an oxidizable oil supplied by the Air Ministry Laboratory, and added to sample *B*(3) in the proportion of 1 quart to 2 gallons of *B*(3). This mixture is denoted by *B*(3) + *X*.

Oil *C* was a thin machine oil. Its composition was not known, but it was known to be a compounded oil.

Oils *D* and *E* were lighter grades of proprietary motor-engine oils. The former was a straight mineral and the latter a hydrogenated oil.

The physical characteristics of these samples are given in Table I.

Table I.

*Physical Properties of Oils.*

| | *A* & *A*(0). | *B*. | *B* + *X*. | *C*. | *D*. | *E*. |
|---|---|---|---|---|---|---|
| Specific Gravity at 60° F. . . | 0·903 | 0·888 | 0·888 | 0·892 | 0·913 | 0·886 |
| Viscosity : | | | | | | |
| (1) Redwood seconds : | | | | | | |
| at 70° F. . . | 2994 | 1711 | 1961 | 301 | 1195 | 1420 |
| at 140° F. . . | 280 | 204 | 189 | 62·8 | 141 | 176 |
| at 200° F. . . | 85·8 | 72·2 | 68·4 | 39·0 | 56·2 | 63·9 |
| * (2) Centistokes : | | | | | | |
| at 70° F. . . | 740 | 422 | 484 | 74·2 | 295 | 350 |
| at 140° F. . . | 68·5 | 49·9 | 46·1 | 13·5 | 34·2 | 42·9 |
| at 200° F. . . | 19·7 | 16·0 | 14·9 | 5·1 | 11·2 | 13·6 |

* The viscosities were measured in Redwood seconds, and were converted to centistokes by means of the I.P.T. Viscosity Nomogram.

In the tables of results of tests, the successive seizures in one bush are numbered consecutively, independently of the oil used. A first run on a bush seldom gives the same seizing temperature as the following runs, and the first seizure of an oil in a bush already "run-in" is generally much higher than the first seizure of the same oil in a new bush. A change to a fresh sample of oil of the same kind is denoted by a change in the figure in brackets, so that the tables of results show the condition of the oil and the condition of the bush.

The tests were commenced on two machines, Nos. 1 and 2. It was found, however, that No. 1 machine gave lower seizing temperatures than No. 2 under the same conditions of test, and so the larger part of the investigation was carried out on No. 2 machine to make the results strictly comparable.

## Tests on No. 1 Machine.

The tests on No. 1 machine consisted of a comparison of the behaviour of oil *A* when blown with hot air during test and when the blowing was omitted, the same bush being used throughout.

The results are given in Table II.

Table II.

*Observations on Oil A in Bush No. 1.*

Machine No. 1: Bush clearance = 0·0077 inch.

| Oil. | Duration of Test, hrs. | Blowing Apparatus. | No. of Seizure. | Coefficient of Friction | | Seizing Temperature, ° C. |
|---|---|---|---|---|---|---|
| | | | | at 40° C. | Min. | |
| *A*(1) | 92 | ON | 1 | 0·0028$_5$ | 0·0008$_5$ | — |
| | | | 2 | 0·0030 | 0·0008$_5$ | 186 |
| | | | 3 | 0·0031 | 0·0007$_5$ | 198 |
| | | | 4 | 0·0033 | 0·0007 | 202 |
| | | | 5 | 0·0034 | 0·0006$_5$ | 222 |
| | | | 6 | 0·0035 | 0·0006 | 231 |
| | | | 7 | 0·0036 | 0·0006 | 241 |
| | | | 8 | 0·0036$_5$ | 0·0006 | 235 |
| | | | 9 | 0·0037 | 0·0006 | 232 |
| | | | 10 | 0·0038 | 0·0006 | 230 |
| | | | 11 | 0·0038$_5$ | 0·0006 | 243 |
| | | | 12 | 0·0038$_5$ | 0·0006 | 242 |
| | | | 13 (*a*) | 0·0039 | 0·0006 | 245 |
| *A*(1) | 39½ | ON | 14 | 0·0036 | 0·0006$_5$ | 205 |
| | | | 15 | 0·0037 | 0·0006$_5$ | 215 |
| | | | 16 | 0·0036$_5$ | 0·0006 | 241 |
| | | | 17 | 0·0037$_5$ | 0·0006 | 250 |
| | | | 18 | 0·0037$_5$ | 0·0006 | 258 |
| | | | 19 (*b*) | 0·0037$_5$ | 0·0006 | 254 |
| *A*(2) | 32 | OFF | 20 | 0·0036$_5$ | 0·0007 | 219 |
| | | | 21 | 0·0036$_5$ | 0·0006 | 226 |
| | | | 22 | 0·0038 | 0·0006 | 257 |
| | | | 23 | 0·0038 | 0·0006 | 260 |
| | | | 24 | 0·0038 | 0·0006 | 257 |
| *A*(3) | 19½ | OFF | 25 | 0·0038 | 0·0006$_5$ | 244 |
| | | | 26 | 0·0039 | 0·0006$_5$ | 256 |
| | | | 27 | 0·0039 | 0·0006 | 259 |
| *A*(3) | 10½ | ON | 28 | 0·0039$_5$ | 0·0006 | 256 |
| | | | 29 | 0·0039$_5$ | 0·0006 | 254 |

(*a*) Bearing surface smoothed with a burnishing tool after this test.
(*b*) Bush degreased in trichlorethylene after this test.

The tests were not continued on this machine, since it was suspected that the loading system was out of order. This was afterwards found to be so, and accounted for the fact that the seizing temperatures were lower than expected. The tests, however, show that any effect due to oxidation is obtained during normal circulation of the oil, without the addition of the hot air blast. The test of oil *A*(2) showed an improvement in seizing temperature of nearly 40° C. by seizing three times, and this might be ascribed either

to oxidation of the oil during circulation, or to the formation of a boundary layer (the test having been started after degreasing the bush), or to a combination of the two.

The test on a fresh sample, $A(3)$, was made on the same bush without degreasing. Now, the second seizure is very close to the maximum, and the maximum possible improvement that may be ascribed to oxidation is reduced very considerably unless the oxidation is nearly completed before the first seizure. Further blowing with hot air did not increase the seizing temperature.

There is a general correspondence between changes in the values of the coefficient of friction at 40° C. ($\mu_{40}$), minimum coefficient of friction ($\mu_{min.}$) and seizing temperature. During the first part of this series of tests the seizing temperature rises and $\mu_{min.}$ falls as $\mu_{40}$ rises. During the second part this correspondence has been upset to a small degree by the alteration in the bush caused by burnishing. From this point the general correspondence remains the same, allowing for a possible variation of 0·0001 in $\mu_{40}$ owing to the rapid rise of temperature at this stage.

It is to be noted especially that the third and fourth parts of the test, in which fresh samples of oil were employed, commence with values of $\mu_{40} = 0{\cdot}0036_5$ and 0·0038, respectively, which are considerably higher than $\mu_{40} = 0{\cdot}0028_5$, at the commencement of the first part of the series. This appears to indicate that all these quantities $\mu_{40}$, $\mu_{min.}$ and seizing temperature are largely affected by the form and condition of the bush and not by the condition of the oil.

## Tests on Machine No. 2.

*Effect of Blowing Oil A with Hot Air before Test.* Two bushes were prepared and tested in machine No. 2. One was lubricated with a fresh sample of oil $A$ ($A(4)$), and the other with a sample which had been blown before test by the method described earlier and is denoted by $A(0)$.

The results of these tests are shown in Tables III and IV.

Table III.

*Observations on Oil $A(4)$ in Bush No. 2.*

Machine No. 2: Clearance = 0·0077 inch.

| Duration of Test, hrs. | No. of Seizure. | Coefficient of Friction | | Seizing Temperature, ° C. |
|---|---|---|---|---|
| | | at 40° C. | Min. | |
| 51 | 1 | 0·0029 | 0·0008 | — |
| | 2 | $0{\cdot}0030_5$ | 0·0007 | 199 |
| | 3 | 0·0031 | $0{\cdot}0006_5$ | 226 |
| | 4 | 0·0032 | 0·0006 | 279 |
| | 5 | $0{\cdot}0032_5$ | 0·0006 | 299 |
| | 6 | $0{\cdot}0033_5$ | $0{\cdot}0005_5$ | 304 |
| | 7 | $0{\cdot}0035_5$ | $0{\cdot}0005_5$ | 310 |

An examination of Tables III and IV shows that oil $A(0)$ reached its best value of seizing temperature after four seizures, whilst oil $A(4)$ improved for seven seizures. Oil $A(0)$, however, had a lower seizing temperature for the

last part of the test than the maximum reached. This result might indicate that oxidation had caused the oil to deteriorate, or that the oil was overblown, so that the best result could not be obtained. When the bush was examined, however, it was found that the apparent arc of contact was not symmetrical along its length, indicating that some undue distortion had taken place in this particular bush, and the next test confirmed this view.

TABLE IV.

*Observations on Oil A(0) in Bush No. 3.*

Machine No. 2: Clearance = 0·0078 inch.

| Duration of Test, hrs. | No. of Seizure. | Coefficient of Friction | | Seizing Temperature, ° C. |
|---|---|---|---|---|
| | | at 40° C. | Min. | |
| 59½ | 1 | 0·0030 | $0·0007_5$ | — |
| | 2 | 0·0032 | $0·0006_5$ | 210 |
| | 3 | $0·0032_5$ | 0·0006 | 245 |
| | 4 | $0·0033_5$ | $0·0005_5$ | 285 |
| | 5 | 0·0036 | $0·0005_5$ | 288 |
| | 6 | 0·0037 | $0·0005_5$ | 266 |
| | 7 | 0·0038 | 0·0006 | 279 |
| | 8 | 0·0039 | 0·0006 | 272 |
| | 9 | 0·0039 | 0·0006 | 274 |

The oil $A(0)$ was next tested in the bush used for oil $A(4)$; this bush had not been degreased after that test, and the carbon deposit on the surface had hardened. The first two runs gave a somewhat low seizing temperature, and on examination it was found that this carbon deposit was cracking. The deposit was removed, and the results were then as expected, the seizing temperature being of the same order as that given by oil $A(4)$ in bush No. 2. The results are given in Table V.

TABLE V.

*Observations on Oil A(0) in Bush No. 2.*

Machine No. 2: Clearance = 0·0077 inch.

| Duration of Test, hrs. | No. of Seizure. | Coefficient of Friction | | Seizing Temperature, ° C. |
|---|---|---|---|---|
| | | at 40° C. | Min. | |
| 44 | 8 | 0·0035 | $0·0005_5$ | 256 |
| | 9 | $0·0035_5$ | $0·0005_5$ | 264 * |
| | 10 | 0·0035 | $0·0005_5$ | 273 |
| | 11 | $0·0037_5$ | $0·0005_5$ | 301 |
| | 12 | $0·0037_5$ | $0·0005_5$ | 308 |
| | 13 | 0·0038 | $0·0005_5$ | 309 |

* Carbon deposit cleaned off bush at end of this test.

From Tables III and V, it is clear that the sample $A(4)$ blown during test and the sample $A(0)$ blown before test give precisely similar friction temperature curves when used in the same bush.

### Tests on Oils *B* and $(B + X)$ in a Prepared Bush.

The seizing temperature of oil *A* had remained practically constant for a considerable period in bush No. 2, indicating that the form of the running surface had reached a condition from which there would be little, if any, change during further running. If another oil were used, any change which might occur in its seizing temperature might, therefore, be ascribed to the oil rather than to the bush. There is, however, the possibility that the boundary layers formed on the bush and/or journal might cause a delay in reaching the true seizing temperature of the new oil. The scheme of the investigation was to run first with oil *B*, which is probably more stable than most oils, then to add an oxidizable constituent to oil *B* and examine the effect upon the seizing temperature. The results of these tests are given in Table VI.

Table VI.

*Observations on Oils B and $(B + X)$ in Bush No. 2.*

Machine No. 2: Clearance = 0·008$_5$ inch.

| Oil. | Duration of Test, hrs. | Blowing Apparatus. | No. of Seizure. | Coefficient of Friction | | Seizing Temperature, ° C. |
|---|---|---|---|---|---|---|
| | | | | at 40° C. | Min. | |
| *B*(1) | 33½ | ON | 14 | 0·0028 | 0·0006 | 247 |
| | | | 15 | 0·0028$_5$ | 0·0005$_5$ | 264 |
| | | | 16 | 0·0029 | 0·0005$_5$ | 267 |
| | | | 17 | 0·0029 | 0·0005$_5$ | 271 |
| | | | 18 (*a*) | 0·0029$_5$ | 0·0005$_5$ | 272 |
| | | | 19 | 0·0033$_5$ | 0·0005$_5$ | 270 |
| | | | 20 | 0·0033$_5$ | 0·0005 | 277 |
| *B*(2) | 14 | ON | 21 | 0·0030 | 0·0005$_5$ | 270 |
| | | | 22 (*a*) | 0·0031 | 0·0005$_5$ | 267 |
| *B*(3) | 5 | OFF | 23 | 0·0030 | 0·0005$_5$ | 270 |
| *B*(3)+*X* | 37 | ON | 24 | 0·0033 | 0·0006$_5$ | 248 |
| | | | 25 | 0·0033 | 0·0006$_5$ | 241 |
| | | | 26 | 0·0033 | 0·0006$_5$ | 247 |
| | | | 27 | 0·0033 | 0·0006$_5$ | 236 |
| | | | 28 (*b*) | 0·0032 | 0·0006$_5$ | 242 |
| | | | 29 | 0·0032 | 0·0006$_5$ | 243 |

(*a*) Bearing degreased after this test.
(*b*) Journal cleaned and polished after this test.

These tests make it clear that with oil *B* any improvement which may be produced by oxidation is completed in the first run, with or without blowing, and that any boundary layer which may be necessary for high seizing temperature is formed during the first run. They also show clearly that the less stable oil $(B + X)$ behaved in a similar manner, but that its seizing temperature was lower than that of oil *B*.

This completed the tests on Bush No. 2, and these tests have yielded no evidence of improvement in oils *A*, *B* and $(B + X)$ due to any oxidation which may have taken place by blowing. They have also shown that in this particular bush the seizing temperatures of the three oils are 310°, 270° and 245° C., respectively.

### Tests of Several Oils in a Bush "Run-in" with Oil B.

A new bush No. 4 was then run-in, using oil *B*, since there was the possibility that the production of the optimum form might depend on the presence of oxidizable constituents in the oil. This bush was successfully "run-in" without blowing with hot air, and for some reason oil *B* for a short period reached a higher seizing temperature than oil *A* (Table VII).

Table VII.

*Observations with Bush No. 4.*

Machine No. 2: Clearance = 0·0078 inch.

| Oil. | Time of Running, hrs. | Blowing Apparatus. | No. of Seizure. | Coefficient of Friction | | Seizing Temperature, °C. |
|---|---|---|---|---|---|---|
| | | | | at 40° C. | Min. | |
| *B*(4) | 35 | OFF | 1 | 0·0023 | 0·0007 | 196 |
| | | | 2 | $0·0024_5$ | $0·0006_5$ | 236 |
| | | | 3 | 0·0025 | 0·0006 | 256 |
| | | | 4 | $0·0025_5$ | $0·0005_5$ | 276 |
| | | | 5 | 0·0027 | $0·0005_5$ | 313 |
| | | | 6 | 0·0029 | $0·0005_5$ | 294 |
| *A*(0) | 35 | OFF | 7 | 0·0041 | 0·0006 | 274 |
| | | | 8 | 0·0043 | $0·0005_5$ | 282 |
| | | | 9 | $0·0043_5$ | $0·0005_5$ | 304 |
| | | | 10 | 0·0044 | $0·0005_5$ | 307 |
| | | | 11 | 0·0044 | $0·0005_5$ | 310 |
| *B*(4) | $13\frac{1}{2}$ | OFF | 12 | 0·0029 | $0·0005_5$ | 269 |
| | | ON | 13 | 0·0029 | $0·0005_5$ | 276 |
| *B*(3)+*X* | $11\frac{1}{2}$ | ON | 14 | 0·0032 | 0·0006 | 277 |
| | | | 15 | 0·0032 | 0·0006 | 272 |
| *C* | $18\frac{1}{2}$ | ON | 16 | $0·0014_5$ | $0·0005_5$ | 222 |
| | | | 17 | $0·0014_5$ | $0·0005_5$ | 223 |
| | | | 18 | $0·0014_5$ | $0·0005_5$ | 219 |
| *B*(4) | 7 | ON | 19 | 0·0030 | $0·0005_5$ | 270 |
| | | | 20 (*a*) | $0·0030_5$ | $0·0005_5$ | 266 |
| *D* | $20\frac{1}{2}$ | ON | 21 | $0·0026_5$ | 0·0007 | 215 |
| | | | 22 | $0·0026_5$ | $0·0006_5$ | 221 |
| | | | 23 | $0·0026_5$ | $0·0006_5$ | 225 |
| *E* | $20\frac{1}{2}$ | ON | 24 | 0·0030 | 0·0007 | 256 |
| | | | 25 | 0·0030 | $0·0006_5$ | 260 |
| | | | 26 | $0·0030_5$ | $0·0006_5$ | 252 |

(*a*) Bearing degreased after this test.

In the previous bush the seizing temperature of oil *A* was 40° C. higher than that of oil *B*. Oil *A*(0) was then run in bush No. 4, but it failed to give a higher seizing temperature than in bush No. 2. Oil *B* was tested again, and gave a seizing temperature of about 270° C. as in bush No. 2. Oil (*B* + *X*) this time gave the same seizing temperature as *B* instead of 25° C. less, as in bush No. 2. Several other oils were then tried in bush No. 4, and in no case was there any evidence of improvement in seizing

temperature by prolonged running, as will be seen in the record of tests on bush No. 4 given in Table VII.

The results in Table VII introduce some inconsistencies: (1) Oil *B* has given a higher seizing temperature than in bush No. 2; this might be due to some small difference in the bushes, but it is not confirmed by the test on oil *A*(0), which gives the same seizing temperature as in bush No. 2. A further test gave the seizing temperature of the same sample of oil *B* as approximately 270° C., as before, and a further test later gave the same result. In view of this it can only be assumed that the high seizing temperature reached in the first series of tests on bush No. 4 was due to some accidental circumstance which afterwards disappeared.

(2) The value of $\mu_{40}$ for oil *A*(0) is extraordinarily high, and for this no explanation has been found. The record of the observations has been carefully examined, and it is quite clear that this high value cannot be accounted for by an experimental error (an error in recording the weights, or by a faulty calibration of the thermocouple). Many other tests have been made on oil *A*, and in no case has so high a value of $\mu_{40}$ been obtained. That it is due to the presence of foreign matter in the oil or to roughness of the journal does not appear to be a reasonable explanation, since so high a seizing temperature was reached. The friction temperature curves for oil A(0) plotted from the results of the tests recorded in Tables V and VII agree extremely closely from 70° C. upwards and separate below 70° C. The temperature rises to 40° C. without artificial heating in about 2 to 3 minutes, so that the determination of the friction at 40° C. is less accurate than at higher temperatures, where the rate of rise of temperature can be controlled. Nevertheless, the observed values of $\mu_{40}$ are generally very consistent.

(3) The test of oil $(B + X)$ now gives the same seizing temperature as oil *B*, instead of 25° C. lower as before. There is, however, a possibility that there was some separation of the mixture in the interval between the tests. Evidence of separation was obtained during the viscosity determination.

As regards the main object of the investigation, the results are consistent. There is no evidence of improvement in seizing temperature and minimum friction by blowing oils *A*, *B*, $(B + X)$, *C*, *D* and *E*. With the exception of oil *A*, all these oils give a seizing temperature very closely in agreement with the maximum on the first test. Oil *A* for some reason requires either one or two seizures before the maximum is reached. The conclusion reached previously is confirmed—namely, that the maximum oxidation effect, if any, is reached during the first run in the machine, and the blowing of the oil with hot air is unnecessary.

Tests in two more bushes were made using a continuous feed of fresh oil *A*, so that the tests were made with any possible cumulative effect of oxidation on the oil eliminated The results of these tests are given in Table VIII.

The agreement between these two bushes is very satisfactory, and the maximum seizing temperatures reached, 294° and 298° C., are nearly as high as that observed for the other bushes (310° C.). These tests both falling lower than 300° C. suggest the possibility that the effect of cumulative oxidation of the oil may be of the order of 10° to 15° C. in 300° C. The number of factors which may affect the seizing temperature and minimum friction is so great, however, that the tests cannot be considered conclusive

to a finer accuracy than 10° C. in the seizing temperature. It is interesting to note that in both the tests recorded in Table VIII the maximum value of $\mu_{40} = 0{\cdot}0038_5$ agrees with the maximum generally reached under oxidizing

TABLE VIII.

*Observations with Continuous Feed of Fresh Oil A.*

Machine No. 2: Clearance = 0·0080 inch.

| Bush No. | Duration of Test, hrs. | No. of Seizure. | Coefficient of Friction | | Seizing Temperature, ° C. |
|---|---|---|---|---|---|
| | | | at 40° C. | Min. | |
| 5 | 15½ | 1 | 0·0032 | 0·0008 | 195 |
| | | 2 | 0·0032 | $0{\cdot}0007_5$ | 215 |
| | | 3 | 0·0034 | 0·0006 | 270 |
| | | 4 | $0{\cdot}0036_5$ | $0{\cdot}0005_5$ | 279 |
| | | 5 | $0{\cdot}0038_5$ | $0{\cdot}0005_5$ | 294 |
| 6 | 7½ | 1 | 0·0034 | $0{\cdot}0006_5$ | 230 |
| | | 2 | 0·0037 | $0{\cdot}0005_5$ | 286 |
| | | 3 | 0·0038 | 0·0005 | 298 |
| | | 4 | $0{\cdot}0038_5$ | 0·0005 | 285 |

conditions. The increase in $\mu_{40}$ cannot, therefore, be ascribed to change in the oil, but must be due to alteration of the form of the running surface.

The change in performance of a journal bearing after several runs to seizure with the same oil is shown in Fig. 6, in which curves are plotted of

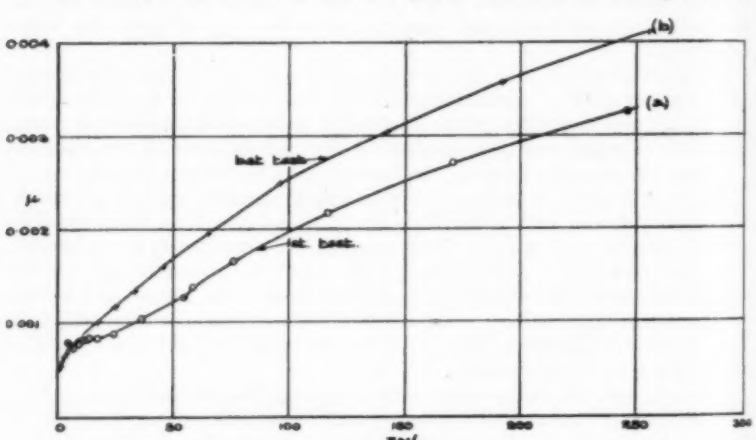



FIG. 6.

coefficient of friction against $ZN/P$. [$Z$ = viscosity in centipoises, $N$ = speed in r.p.m., $P$ = load in lb./in.².] Curve (*a*) represents the first run to seizure, and curve (*b*) a run after the optimum condition has been reached; they are plotted from observations made during the first and last tests given in Table III. In curve (*a*) there is a sudden change in the slope of the curve

at $ZN/P$ equals about 50. This does not necessarily indicate a cessation of fluid film conditions, since an increase in eccentricity might account for such a change. Curve (*b*), however, shows a continuous curve without any sudden change in slope down to a value of $ZN/P$ less than one. This appears to indicate that fluid film conditions have been maintained nearly to the seizing temperature.

The higher friction of the last test at higher values of $ZN/P$ is ascribed to a change of form of the bush giving a smaller effective clearance.

## Conclusion.

(1) The increase in seizing temperature and decrease in minimum friction produced by running a bearing periodically up to seizing temperature in oxidizing conditions, is not due to any great extent to a change in the oil, being almost entirely accounted for by changes in the form and surface finish of the bush.

(2) The optimum form of bush can be produced by either of the oils *A* and *B*.

(3) With the four oils, *B*, *C*, *D* and *E*, the maximum seizing temperature may be reached during the first run in a bush already "run-in." Oil *A* throughout these tests required at least one seizure before the maximum seizing temperature was reached.

(4) When a bush has reached the "run-in" condition fluid film lubrication appears to be maintained almost up to seizure.

## Acknowledgments.

The work described has been carried out in the Engineering Department of the National Physical Laboratory for the Air Ministry, under the general supervision of the Lubrication Panel of the Engine Sub-Committee of the Aeronautical Research Committee. The authors desire to record their thanks to the Committee for permission to publish the results, and to Dr. H. J. Gough, F.R.S., Superintendent of the Engineering Department, N.P.L., for his interest and encouragement in the research.

## APPENDIX.

### Note on "The Effect of the Addition of Ethyl Fluid to Castor Oil."

In the experiments recorded in Aeronautical Research Committee R. & M. No. 1517 (King and Jakeman) very high seizing temperatures were obtained for a mineral oil in a bush which had previously been run with castor oil doped with ethyl fluid. At the beginning of the present investigation further experiments were made to produce an improved running surface by the same means.

The bushes used were lathe bored and polished with emery paper, being similar to the bushes called *B* finish in R. & M. No. 1517.

The tests were made on an N.P.L. journal friction machine, the conditions of test being the same as in the present investigation, except that the oil was filtered through a gauze instead of through wash leather. The ethyl fluid was stated to contain 60 per cent. by volume of lead tetra-ethyl and 40 per

cent. by volume of ethylene dibromide, with a small volume of colouring matter. It was added to castor oil to the extent of 0·26 per cent. by volume.

Two bushes were run and gave the following results :—

*Bush No.* 1.

This was run to seizure with pure castor oil. Ethyl fluid was then added, and the bearing run for several days at about the temperature of minimum friction, after which the seizing temperature was obtained and the bush examined. Pure castor oil gave a minimum coefficient of friction ($\mu_{min.}$) of 0·0009 and a seizing temperature of 196° C. With doped castor oil $\mu_{min.}$ fell from $0{\cdot}0010_5$ to $0{\cdot}0009_5$ during 48½ hours, and the seizing temperature at the end was 138° C. Visual examination of the bush showed that the surface condition was unsatisfactory.

*Bush No.* 2.

After about 20 hours running with pure castor oil, two runs to seizure were made which gave seizing temperatures of 241° C. and 231° C. and $\mu_{min.} = 0{\cdot}0007_5$. This was followed by 49½ hours running with doped castor oil at about the temperature of minimum friction, a seizing temperature being taken at the end of this run. $\mu_{min.}$ decreased from 0·0010 to 0·0009 and the seizing temperature was 162° C. The pure castor oil was replaced, and two further observations of seizing temperature were made. These were 186° C. and 215° C. Visual examination after the run with doped castor oil showed that the surface was not so good as at the end of the run with pure castor oil. The two final runs with pure castor oil appear to indicate that the surface is again improving as soon as the ethyl fluid has been removed.

These tests show that the addition of ethyl fluid to castor oil causes an increase in the minimum coefficient of friction, a decrease in the seizing temperature and visible deterioration of the bush surface.

# OBITUARY NOTICES.

CARLOS BERNARD MCKEEVER, one of the founder members of this Institution, died in August 1936. He was an early pioneer of British enterprise in foreign ventures. In his early work he was associated with Sir Boverton Redwood.

The death of " Rosey " Rosenplaenter (who later changed his name to McKeever) breaks one of the few human links with the early pioneering days of the nineties and first years of the twentieth century.

Rosenplaenter was born in the early sixties in the United States of America, and was an American citizen until about ten years ago, when he took his mother's patronymic McKeever, and also became a British subject.

Young Rosenplaenter accompanied his parents when they returned to Germany, where he completed his education at Heidelburg University, specializing in chemistry. He first became connected with British oil men, especially Boverton Redwood, through Alfred Seward in Hamburg, where his father had an office.

He will be remembered for his pioneering work in Persia, when, in 1903, he joined G. B. Reynolds at Chiah Surkh for the late Mr. D'Arcy. The then British Minister at Teheran, the late Sir Arthur Hardinge and one of the " Persian " Churchills, who accompanied him as Secretary, when returning to Persia in 1905, spoke very highly of Rosenplaenter's work in Persia, and the late C. A. P. Stewart, geologist, often talked of the great difficulties and hardships which were endured and overcome by Rosenplaenter and his companions during the first year of their work at Chiah Surkh. According to Stewart, who was then acting as Rosenplaenter's assistant, the native nomad shepherds had no conception of working for wages, and were only persuaded to do earth work by being given prizes which varied with the amount of earth that they moved. In fact, Rosenplaenter inaugurated piece work with these shepherd folks.

The heat, especially trying in 1903, was mitigated by driving into the side of the hill and there constructing underground an office and one or two living-rooms, which were made quite decent-looking by covering the walls with local plaster of Paris.

Another very trying element of the life at Chiah Surkh was the bad water, which contained, among other ingredients, a large percentage of gypsum. This affected both Rosenplaenter and Stewart so badly that they were unable to return to Persia for another summer (see *Naft Magazine*, August 1934).

McKeever's death will be regretted by many members of the Institution, who will recall his generous hospitality, his genial manner and his invariable kindness to young men starting their careers in the Petroleum Industry.

The compiler of these notes, who, in 1906, was his personal assistant during the beginning of the petroleum exploratory work carried out by S. Pearson & Son on the Isthmus of Tehuantepec, Mexico, will always owe

a debt of gratitude to McKeever for his forbearance and guidance in work, and kindliness during occasional days of relaxation.

S. H. C.

THEODORE SPENCER (Member) died on 23rd April, 1937, at his home in Woodingdean, Sussex. He was 53 years of age. He had been ill for some months, but the end came so suddenly that many of his friends learned of their loss only some little time after it had occurred.

Born in 1883 and educated at Brighton College, Spencer arrived on the Baku oilfields—after serving an apprenticeship in the Mercantile Marine—in the early part of 1902.

He was engaged for the most part in drilling operations in Russia and in Roumania until 1916, when, after a few months in the Royal Navy, he joined the Aeronautical Inspection Directorate.

Shortly after the Armistice he was engaged with Messrs. S. Pearson & Sons in their Chesterfield drilling campaign. In 1920 Spencer was appointed Instructor in Oil-Well Drilling at Birmingham University. Subsequently he was employed in the Argentine, in the U.S.A., and again in Roumania.

He was known therefore to a large number of members of the Institution, of which he became an Associate Member in 1914.

It would be hard to appraise too highly the candid and kindly characteristics of this man. His keen interest in art and his devotion to animal welfare—apart from his life-work—brought him in touch with all kinds and conditions of men, amongst whom his sincerity and manly decency commanded respect, and often gained for him lasting friendships.

Spencer could not tolerate affectedness; truth and simplicity he valued dearly.

Be it enough to add that his absence will be suffered with an abiding affection for a good man.

W. E. G.

# THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

## DEEP DRILLING PROBLEMS.

THE One Hundred and Seventy-sixth General Meeting of the Institution—a Conference on Deep Drilling Problems—was held at the House of the Royal Society of Arts, London, on Tuesday, May 4th, 1937.

LT.-COL. S. J. M. AULD, O.B.E., M.C., D.Sc., President, was in the Chair.

The following papers were considered by the Meeting :—

"Geological Aspects of Deep Drilling Problems," by W. E. V. Abraham. (*See* p. 378.)

"Preparation and Control of Mud Fluid for Pressure Drilling Conditions," by J. T. Evans. (*See* p. 391.)

"Drilling of a Deep Pressure Test in India," by G. F. Wilson. (*See* p. 401.)

"Notes on Deep Wells Drilled in Iran," by G. W. Colvill. (*See* p. 408.)

"Deep Well Drilling," by G. Elias and Members of the Roumanian Branch. (*See* p. 412.)

"A New Type of Threaded Connection for Oil Well Casing," by W. M. Frame. (*See* p. 422.)

The Chairman asked Mr. C. A. P. Southwell to open the meeting.

MR. SOUTHWELL said that the Council of the Institution had given very serious consideration to the arranging of meetings of the Institution in London at which members home on leave from the various producing areas could present papers of practical and scientific interest, and which would provide suitable opportunities for meeting and discussing the many points of interest. It was hoped that this meeting on Deep Drilling would be followed by meetings each year at which members would illustrate their discussions with cine kodak films, lantern slides, or photographs.

Mr. Southwell said that he proposed to show a film illustrating some of the deep drilling which had been undertaken in the American fields, and certain slides which illustrated more particularly the various methods of increasing the speed of drilling and the movement of equipment so that the cost of deep drilling could be reduced.

*(Cinematograph film showing drilling technique in certain of the American fields, and lantern slides illustrating methods of increasing speed of drilling and movement of drilling equipment were shown.)*

The opportunity had been taken by several of the Branches of the Institution to discuss deep drilling problems, and they would all be interested in the contributions which would be discussed later. He had, he said, a contribution to read which gave the details of certain deep wells which had been drilled in Iran. This contribution had been prepared by Mr. G. W. Colvill, the Chief Drilling Superintendent in Iran of the Anglo-Iranian Oil Company. Unfortunately, Mr. Seamark, who was responsible

for the drilling technique, was abroad, otherwise Mr. Southwell had hoped that he would be present to amplify the contribution which Mr. Colvill had prepared, especially in connection with some of the pressure drilling difficulties which had been successfully overcome in Iran.

(*Mr. Southwell then read the contribution by Mr. G. W. Colvill, Chief Drilling Superintendent in Iran of the Anglo-Iranian Oil Company.*)

In concluding these details of certain deep wells which had been drilled in Iran, Mr. Southwell said that the drilling staff had been able to complete these wells without any great difficulties only by the most careful attention to detail, especially in regard to the characteristics of the circulating mud and to the carefully controlled weight on the bit, and the difficulties which might have arisen had been averted by this attention to detail.

In one respect, however, Mr. Southwell said, they had not had conditions which certain operators had experienced in other fields; he referred to high temperatures at depth. He understood that temperatures as high as 240° F. had been recorded in some wells, but the temperatures in the wells reviewed had not presented any great difficulty with the cementing operations.

Mr. Southwell felt that the record was an interesting one, and would be useful to other members of the Institution who were contemplating deeper wells than had already been drilled.

## *DISCUSSION.*

THE PRESIDENT remarked that the members had before them three papers which had already been read before Branches. It had been hoped that Mr. Abraham would have been present that day, but he had been prevented from doing so, and Mr. Ellis had been good enough to accept the Council's invitation to report on those papers as they stood.

MR. B. J. ELLIS, in the absence of the authors, summarized the papers by Mr. W. E. V. Abraham, Mr. J. T. Evans, and Mr. G. F. Wilson, emphasizing the principal points for discussion.

MR. G. W. LEPPER congratulated Mr. Ellis on the able way in which he had summarized the papers at short notice in the absence of all the authors.

Up to just over a year ago he (the speaker) had considerable interest in some of the wells referred to in the papers from the Burmah Branch and in the research undertaken in connection with them. So far as he could tell from the reports regarding the deep well in Assam, he had not in his experience come across anything quite like it. Whether some of the deep wells which had been put down comparatively easily in Iran and elsewhere had encountered much gas and salt water he did not know, but it was possible that the presence of these fluids gave a " spear-head "—if he might so describe it—to the abnormal pressure obtaining in the strata and made it much more troublesome.

With regard to the actual cause of the abnormal pressure, Mr. Abraham believed that a case had not yet occurred where pressures in deep wells were greater than the maximum estimate of the earth pressure likely to

obtain at that depth. That, in Mr. Abraham's opinion, seemed to be a strong point in favour of the suggestion that earth pressure was the cause. The speaker read the other day however that there had been cases where abnormally high pressures at certain levels had been succeeded by lower pressures and followed again by higher ones. Unfortunately, he had been unable to track down the details. If this report were true, it seemed to run counter to the theory that earth pressures prevailed continuously below some critical level depending on local conditions.

With regard to the short paper on the manufacturers of deep drilling muds, by Dr. J. T. Evans, Dr. Evans was one of the Burmah Oil Company's Fields Chemists who had been responsible for the preparation of many different types of drilling mud. Mr. Ellis had mentioned that a considerable "tome" on the subject of muds by "Mr. Evans" had recently appeared. The speaker would like to remove any possible misunderstanding: the Mr. Evans, who with Mr. Alexander Reid (also of the Burmah's Fields Chemical Staff) was responsible for the volume on Drilling Mud, was Mr. Percy Evans, of the Burmah's Geological Staff.

The speaker had seen this "tome" recently, but had had the privilege of being in touch with the work almost from its inception. Mr. Ellis modestly refrained from mentioning the fact that he himself was responsible for suggesting that the paper should be prepared for this Institution. As the task progressed, almost concurrently with the drilling of the deep well in Assam and with the solution by painstaking research of problem after problem in connection with mud manufacture, it became evident that the limits of an ordinary Paper would be exceeded. When first completed it was found to be altogether too big to go within the compass of this Institution's *Journal*. A determined attempt was made to cut it down, and then it was, for various reasons, finally published as a volume of the *Transactions* of the Mining and Geological Institute of India, a body almost as keenly interested in oilfield technology as in coal and metalliferous mining practice.

The work was published in a very convenient form, and in his opinion would be extremely useful for any technologist engaged in drilling under conditions where mud problems were likely to arise. He believed that he was right in saying that it was now possible through their own Institution to obtain copies of the volume in this country. As he was now no longer a colleague of the authors, he could speak as an outside critic, and had much pleasure in commending a very useful publication.

MR. ASTBURY stated that the Mining and Geological Institute of India had sent him some forty or fifty copies of the work by Dr. Percy Evans, and these were available for sale at the Institution offices, the price being 19*s.* 6*d.*

MR. A. BEEBY THOMPSON congratulated Mr. Evans on the submission of an unusually interesting paper, and said that those present were under a debt of gratitude to Mr. Ellis for presenting the paper so lucidly. Mr. Lepper in his remarks had hit upon one of the most important points raised in the paper which fixes a critical depth where hydrostatic pressure is replaced by rock pressure. Many years ago he proceeded to collect information about deep well pressures, and at that time it was rarely

possible to find a single instance where oilfield pressure exceeded those that could be attributed to a hydrostatic head, but in recent years pressures had been credibly recorded which far exceeded those due to a hydrostatic head, and these have been attributed to the weight of overburden. One had always to consider the possibility of striking inherited pressures due to former land elevations far in excess of those existing to-day, for thousands of feet of beds must have been eroded from some structures which must have caused at one time hydrostatic pressures greatly in excess of those that could now be formed hydrostatically.

Then was it wise to disregard the question of compressional forces which must have caused exceedingly great pressures in the lower parts of tight folds? He was not prepared to say that rock pressure was not a frequent cause; but he did think that exceptionally high compressional pressures might be generated, and if it is admitted that lower pressures are met with in wells beneath zones of very high pressure, as in a number of cases in Burmah, it seems that compressional or inherited pressures must be held responsible.

No mention was made in the paper of the possible continuous formation of gas. Many still believed that if drilling in the mother series of beds, there was the possibility of gas being generated and pressures being raised far in excess of those due to earth pressures. That, of course, was a chemical problem about which it was only possible to theorize at present, but it seemed a reasonable possibility.

With regard to rock pressures, it was known in hydrological work that surface-applied pressures could be transmitted through sediments, and in some of the American publications there were recorded cases where the effect of a train passing over the ground was registered in wells by a slight movement of the water level. He considered that this question of increasing pressure with depth was very important indeed, because, as Mr. Ellis had said, it looked as if their drilling depths were going to be limited by the means available for drilling against these pressures. If Mr. Abraham was correct in his views—which he thought very rational—that these very high pressures might be bled off, then it simplified the process of drilling down into very high pressure ground where it might otherwise be impossible. Such pressures can be bled off at times by a remarkably small release of fluid.

Mr. B. J. Ellis mentioned that it might be worth while citing in this connection a few figures. He found that the ultimate breaking stress of various rocks under compression was: granite 15,000 lb. per sq. in., marble 10,000 lb. per sq. in., limestone 7000 lb. per sq. in. and sandstone 8000 lb. per sq. in. The weight per cubic foot was: granite 170 lb., limestone and marble 168 lb., sandstone 151 lb., and shale 162 lb. There was a mountain in India which was 29,000 ft. high. If it were assumed to be a cone, then its weight would be that of a cylinder of one-third its height, say 10,000 ft., and the pressure per square inch on the bottom end of the cone would be somewhere about 10,000 lb. If it was granite it would stand such a pressure, if it was limestone the rock would pulverize because limestone crushed up at 7000 lb. per square inch. It was obvious, therefore, that Mount Everest was not held up by the strata immediately underneath,

but that the weight was spread over a much greater surface of the earth. One could quite imagine that in a syncline unconsolidated tertiary strata would transmit their weights down to the lowest stratum, but where the formation was arched, the theory that formation pressures were due to the weight of the superincumbent strata seemed open to doubt.

Colonel S. J. M. Auld said that he felt sure he was expressing the views of the audience in congratulating Mr. Ellis on the very able manner in which he had presented the three papers which had been read before the Burma Branch of the Institution.

Mr. C. Dabell said that to his mind the pressures were far more likely to occur from lateral earth movement than from superincumbent strata. If the pressure was from the superincumbent strata, one would expect to find, in many parts of the world, wells collapsed. He knew of wells which had in course of time been abandoned, and then in later years found that they had gone to one side at the bottom, presumably by lateral movement; but he had never heard of wells which had completely collapsed, though this should be anticipated were the weight of superincumbent strata effective.

Dr. J. A. L. Henderson said that he thought the discussion of this series of papers was a very useful event, and he paid a tribute to the enterprise of the Council in arranging it. The papers raised a great many points concerning deep drilling which required attention at the present time. So far as the preliminary discussions were concerned, dealing with the effect of temperatures and pressures, these questions had been much discussed by those who had drilled deep wells, for many years past, and had been tested in various ways. The great depths of modern drilling enhances their importance and interest. He, himself, had always had a leaning towards the interpretation of the pressures as associated with earth pressures and temperatures—that is to say, vertically through the superincumbent rock, and laterally through regional movement. In certain cases, due to denudation, what were called fossil pressures by one of the authors had been preserved beneath relatively shallow cover. He had also tried to test the question by drilling through major unconformities, but had not found any conclusive evidence on the subject. He had found gas and oil pressures considerably exceeding the calculated hydrostatic pressure, but in the case of salt-water flows from the same beds much lower pressures were found.

Mr. L. J. Wilmoth said he felt that a debt of gratitude was due to the authors of these papers and the companies that had permitted the disclosure of the information. In approaching the question of pressure in the various fields, it seemed to him that the only way they were likely to arrive at a satisfactory explanation was by grading their fields into geological types. It was no use making a comparison, say, between one of the fields in America in the older rocks and a tertiary field such as they had in Burma. In the fields in the older rocks there was a stability of condition which was absent as a rule in the younger tertiary fields. Take, for example, Assam and Burma. There was very little doubt that, geologically speaking, there was not a condition of absolute stability in those regions. There was still a

definite movement in progress. The geological structures had not yet reached a stable condition; they were still being built, and that must bring in the factor of lateral compression which in itself introduced a very important point other than the superimposed weight. In the old fields he thought one had mainly superimposed weight and perhaps a certain amount of fossil pressure. In the younger fields there was often, along with other factors, the compression weight of actual geological movement which was in progress. When a comparison was made, care should be taken to distinguish between fields subject to different geological conditions, for otherwise conclusions would be reached which would mislead them and be of no help whatever to the drilling people.

Dr. Henderson said that he appreciated the point raised by the last speaker, but it could not be suggested that the older rocks were lacking in evidence of the influence of lateral pressure at the present time.

Mr. P. T. Cox said that a point which deserved to be stressed was the strength or competency of the formations concerned. The Pirgah No. 2 well which Mr. Southwell had described was drilled through a highly incompetent group of beds, the Lower Fars, consisting of marls, salt and anhydrite. Trouble with squeezing in of the sides of the hole became apparent only where a zone of crushed and faulted beds was entered at 6000 ft. depth—that is, where the strength of the beds was greatly reduced. Any fluid trapped within this zone must have been under a pressure considerably higher than normal hydrostatic head, though no such show was proved. Similarly, water or other fluids trapped within porous beds in groups which were incapable of supporting the weight of superincumbent strata would be expected to be at higher pressures than the existing, or even a past hydrostatic head. Even where not crushed and rendered so incompetent that the walls of a well readily yield to the weight of overburden, the Lower Fars in S.W. Iran evidently does, in the course of geological time, impart abnormally high pressures to waters held in thin limestones or sandstones in the series. In both the Masjid-i-Sulaiman and Haft Kel fields Lower Fars shows frequently are at higher pressures than that of fluids contained in the underlying more competent Asmari Limestone.

Mr. C. Dabell asked why Mr. Ellis feared to let the pressure off these high-pressure wells.

Mr. Ellis said that it was not a question of being frightened, but of not being able to do it. Various methods had been tried, and did not seem to work in soft strata. They could let the pressure off, but the hole caved at the same time.

Mr. Dabell said that there must be a pressure which would be sufficient to hold up the sides of these holes—he thought Mr. Ellis had suggested something like 6000 lb. to the square inch as the breaking stress under compression. Would a 3000 lb. per square inch pressure be sufficient to hold up the sides of the holes?

MR. ELLIS replied that if any of the pressure were taken off the top, the hole started to cave in.

CAPTAIN D. COMINS said that Mr. Abraham, in the discussion which took place in the Burma Branch, had met certain criticism of his interesting and provocative paper by using the analogy of a sparrow alighting on a girder, causing even the strongest girder to sag. He might employ a similar analogy. The sparrow—an intelligent sparrow—might be watching the pressure gauge of a boiler blowing off at a steady pressure. After a time, being interested, the sparrow decides to investigate, perches on the safety-valve, and notices that the pressure gauge begins to rise. He therefore concludes that he is the source of the increased pressure in the boiler—a logical but nevertheless erroneous deduction exploded eventually by the boiler itself!

Similarly, in the speaker's view, superincumbent strata were seldom the primary source of pressure in a reservoir, but, when plastic, acted as the safety-valve of the reservoir, and therefore as a competent cap-rock in a wider sense than usually understood. In plastic beds, seepages through fissures formed by the reservoir pressure exceeding the earth pressure would tend to seal themselves off when the reservoir pressure had been reduced by such seepages to the earth pressure or lower.

Exceptionally however he agreed that where the reservoir beds were thin or lenticular or unconsolidated, it was possible for the reservoir pressure in them to be due primarily to the weight of the superincumbent strata; but in thick rigid and continuous reservoirs, such as the limestone reservoirs in Iran, the primary source of pressure was undoubtedly hydrostatic.

Mr. Abraham had claimed that in the case of rigid reservoirs the pressure was built up by squeezing out of fluid from the superincumbent strata into the reservoir rock. He had not however adequately met the criticism made by Mr. J. Bayliss at the Burma I.P.T. meeting that that would not apply in a gas reservoir. He (the speaker) entirely agreed with this view. The amount of fluid which would have to be forced into a reservoir to put up the pressure of an extensive gas dome by even a few hundred pounds would be far too great.

He disagreed with any general application, other perhaps than in thin bedded flat reservoirs, of Mr. Abraham's major conclusions: (1) that as a general rule reservoir pressures in shallow fields correspond to hydrostatic pressure and in deep fields to earth pressure, and (2) that if at any given depth reservoir pressures approximating to earth pressures are encountered, the same relation is probable at greater depths.

On the contrary, in the case of structures with considerable closure it was quite possible for the reservoir pressure at the top of the structure—which might be quite shallow—to be as high as the earth pressure, even though the primary source of the reservoir pressure was hydrostatic.

Under these circumstances, at greater depths down flank the ratio of reservoir pressure to earth pressure would be progressively less—owing to the differences in specific gravity between earth, gas, oil and water. At and below oil–water level the reservoir pressure would be the hydrostatic pressure. These were the pressure conditions on the Masjid-i-Sulaiman field

before production started, and it would be remembered that in part of the crestal area of this field the cover was only some 700 to 800 ft.

The diagrammatic sketch (Fig. 1) illustrated how reservoir pressure may be 50 per cent. of the earth pressure at oil–water level; 75 per cent. at gas–oil level and 100 per cent. at the point of least cover—in this case the crest maximum of the structure as the ground is shown flat for simplicity.

On the subject of temperatures, Mr. Abraham had said that as a general rule the temperature gradient "tends to be higher close to folded strata than elsewhere." Geothermal evidence in Iran was, of course, entirely from wells, and therefore mainly in folded strata. Great variations of gradient were observed, but the evidence was so conflicting as to preclude any general conclusions. Over the greater part of the Masjid-i-Sulaiman field gradients were much lower in the crestal area than down the flanks. In the crestal area at 1° 250′ the gradient was substantially less than

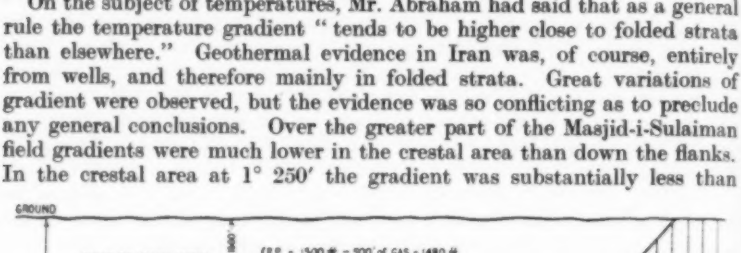

GROUND
POINT OF LEAST COVER
GAS
OIL
WATER
5000
800
3000
R.P. = 1500 # - 500' of GAS = 1480 #
E.P. = 1500' of EARTH = 1500 #
RATIO RESERVOIR PRESSURE : EARTH PRESSURE = ABOUT 100 %
R.P. = 2500 # - 3000' of OIL = 2500 - 1000 = 1500 #
E.P. = 2000' of EARTH = 2000 #
RATIO RESERVOIR PRESSURE : EARTH PRESSURE = 75 %
R.P. = 5000 of WATER = 5000 x 0·5 = 2500 #
E.P. = 5000' of EARTH = 5000 #
RATIO RESERVOIR PRESSURE : EARTH PRESSURE = 50 %
FOLLOWING FACTORS ASSUMED AS ROUGH APPROXIMATIONS :-
PRESSURE PER FT. OF SUPERINCUMBENT STRATA = 1 #
EDGE WATER = 0·5 #
RESERVOIR CRUDE = 0·33 #
DOME GAS = 0·04 #

FIG. 1.

Mr. Abraham's low limit of 1° 180′. The highest gradient in his experience was 1° 50′, and he had not previously heard of gradients approaching Mr. Abraham's high limit of 1° 20′. It would be interesting to have further details of this observation.

None of the authors had mentioned the recent tendency for a rather abnormal number of gas-fields to be found by deep drilling. These gas-fields seemed to carry more distillate or light oil than would be expected to be forthcoming as a condensate from dry gas in equilibrium with crude at the high pressures obtaining in these fields. If any member present had any experience or ideas on this subject, it would be of considerable interest.

MR. B. J. ELLIS said that Captain Comin's diagram was extremely interesting, but it did not meet the point he had made, that they found moderate pressures at the top of the dome, but when they reached stratagraphically greater depths, the pressures changed from the equivalent of the hydrostatic head to approximately twice that of the hydrostatic head. Mr. Abraham was not theorizing in this respect, he was setting down the actual facts which were observed at depths from 5000 to 8000 ft. in wells in Burma and India.

Mr. C. P. Southwell, in concluding the discussion, said that he wished to [illegible] his congratulations to Mr. B. J. Ellis of the Burmah Oil Company for introducing the papers which had been presented by his colleagues. He also wished to pay special tribute to the mud research which Mr. Evans and his colleague had recently published. This publication in the *Transactions* of the Mining and Geological Institute of India, which they were all very glad to see, was a large volume which would repay careful study by all members of the Institution who were connected in any way with drilling problems. He understood that it had been suggested that this report should be printed in the *Journal* of the Institution, but, having read it and realizing how large it was, and how many numbers of the *Journal* would be required for its publication, he appreciated why this had not been possible, and also why it was not possible for the report to be reduced. It was, he said, a work which the Institution would take great pride in as a contribution from two of its members.

The question of deep drilling, Mr. Southwell said, covered too wide a sphere for satisfactory discussion in the short time which had been available; but, nevertheless, the meeting had provided opportunity for members of the Institution to meet and discuss certain of the problems involved in which they were particularly interested. The many aspects of the problem could be described alliteratively as mainly muds, metals, and men, and, although the metallurgical knowledge in regard to casing and drill-pipe for these great depths was perhaps lagging behind, there was little doubt that the specifications required would be forthcoming when deeper drilling was more general, and no difficulty in this connection had been experienced in the wells which the Anglo-Iranian Oil Company had drilled. Pumps capable of dealing with high pressures were a matter on which considerable thought was necessary, but, as happened in so many oil problems, thought was given only when the problem arose and provision had to be made.

It was, Mr. Southwell felt, very remarkable, when one realized the large percentage of the world's production which America provided, that they did not have more of the pressure-drilling difficulties at depth which Mr. Ellis had commented on, and with which he in Burma and many in other foreign fields had to contend.

The discussion had diverted from the mechanical problems of deep drilling to geological and physical problems of what would be found at great depth. Recent results indicated a greater proportion of gas-fields at depth, and, whilst Mr. Southwell did not know if this was a coincidence or whether it had some scientific reason, he felt that it was a problem worthy of discussion by the Institution on theoretical grounds, taking into account the geological, physical and chemical aspects, to see if the results obtained had theoretical reasons for the presence of more gas than petroleum fluid in the structures at the greater depths which were now being drilled.

In conclusion, Mr. Southwell hoped that the present meeting would stimulate similar meetings next year, and that the Branches would co-operate and provide films or slides in order to assist with the discussions and make them of much more interest to all concerned.

*The Meeting then terminated.*

# GEOLOGICAL ASPECTS OF DEEP DRILLING PROBLEMS.*

By W. E. V. Abraham, A.R.C.Sc.I., B.Sc. (Member).

Summary.

The most important features influencing the drilling of very deep wells (as opposed to "ordinary" wells 2000 feet or 3000 feet in depth) are not

(*a*) the increased distance between points of development and of application of mechanical power (this is almost entirely an engineering problem),

nor (*b*) the depth/temperature gradient (this is of much theoretical interest, but presents only minor difficulties in respect of cementation and mud control),

but (*c*) the fact that, in some parts of the world at least, fluid pressures at depth increase not in accordance with the corresponding hydrostatic head, but in accordance with more than double this head.

Possible causes for (*c*) are considered in this Paper, and it is regarded as most probable, on present evidence, that the pressures of more than double the corresponding hydrostatic head which are sometimes encountered are simply the corresponding "earth pressures" due to the weight of superincumbent strata.

Some practical consequences of this theory, if it be accepted, are indicated, and in particular it is suggested that where fluid pressures of "earth pressure" value are known to exist at any depth, we ought to be prepared for correspondingly higher pressures, still in accordance with "earth pressure," at greater depths.

There are three chief differences between the drilling of a deep well, say to 8000 or 9000 feet, and the drilling of an "ordinary" well to 2000 or 3000 feet :—

(A) In a deep well the point of application of power, *i.e.*, the bit, becomes very remote from the source of mechanical power.

(B) In a deep well, temperatures are higher.

(C) In a deep well, pressures are higher.

## (A) Increased Length of "Transmission Shaft."

The problems involved in the actual transmission of power, by means of drill pipe of necessary strength, are purely engineering ones, and therefore outside the scope of this paper, but there are a few geological or partly geological consequences of the increased depth as such, which perhaps deserve a passing reference independently of the effects of increased temperatures and pressures, which will be considered separately :—

(i) It usually happens that at very great depths all our geological forecasts, both as to structure and as to depths at which particular

* Paper presented to the Burma Branch, Institution of Petroleum Technologists, at Yenanyaung, 28th August, 1936, and in London on 4th May, 1937.

horizons will be met, become much more uncertain than when we are concerned with shallower wells. Because of this difficulty geophysical methods are being more and more used in connection with such problems.

(ii) It frequently happens that the strata being drilled through become harder, more compact, or tougher, with increasing depth. This is, of course, mainly an effect of past, if not of present, pressures, and of age.

(iii) At great depths the actual time taken to pull the drill-pipe "transmission shaft" out of the hole (as often as this becomes necessary) frequently imposes a limiting condition on operations (*e.g.* coring) which other geological factors would make desirable.

### (B) Increased Temperatures.[1]

We all know that, as we descend a mine, or drill a well, we encounter a rising temperature gradient. Without considering in any detail the evolu-

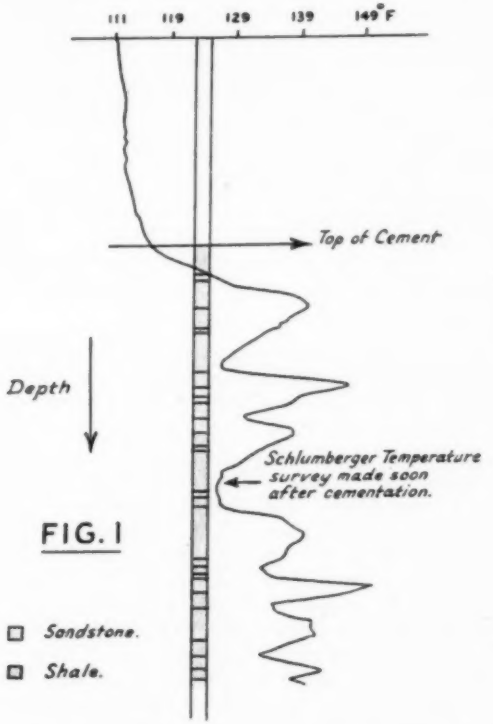



FIG. 1

tion of the earth as a part of the solar system, we may regard the earth, like the sun, as a gradually cooling body, the continuous loss of heat from the

interior of the earth being to some extent counterbalanced by the generation of heat from the disintegration of radioactive elements. What is perhaps not so well known is that the temperature gradient is by no means the same in different places, and that as a general rule it tends to be higher close to folded strata than elsewhere. Even on different anticlines in the same region the temperature gradient may vary, and in some parts of America a regional variation in temperature gradient has been noticed. A fairly common oilfield temperature gradient is one degree Fahrenheit for every 50 or 60 feet of depth, but gradients as different from this as one degree for every 20 feet and one degree for every 180 feet are on record.

Sufficient data are not available to allow of the formulation of any general theory of temperature gradient variation, and, strangely enough, such evidence as is available does not suggest that gradients in regions known to

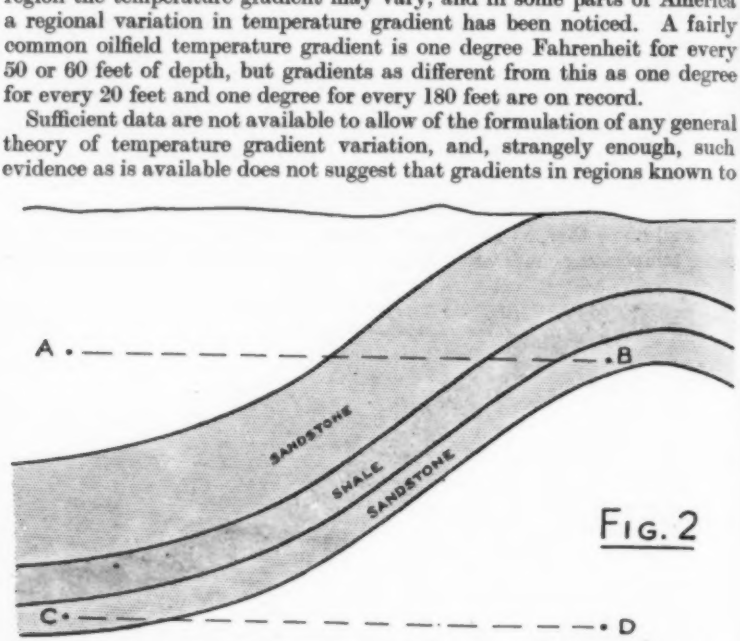



FIG. 2

Considering the levels AB and CD, B can obtain heat both from D, across the bedding, and from C, along the sandstone which is a better conductor than the shale. A obtains heat only across the bedding, from C, and must therefore have a lower temperature than B.

be rich in radioactive substances are abnormally high. If, however, we confine our attention to the problem of why the temperature gradient on an anticline should be greater than in the neighbouring syncline, we find that a simple explanation is available in the fact that in stratified rocks conduction of heat must always be easier "along the bedding" than "across the bedding," and that, in consequence, heat is "led up" into an anticline along certain strata from greater depths in the synclines. As an example, Schlumberger temperature surveys, taken soon after cementation (Fig. 1), furnish a very beautiful proof of the fact that a bed of standstone conducts heat away laterally more rapidly than a bed of shale, and it is clear that, qualitatively at least, this provides an adequate explanation for the existence of a higher temperature at point B than at point A in Fig. 2. This effect may in some cases be influenced by circulating waters. A few instances are known where temperature gradients have changed rather abruptly

close to the edge of an oil deposit, and it would seem possible that these changes have been influenced by the actual conductivity of the oil. Similarly, the sudden changes in temperature gradient which have been noted over salt domes are almost certainly intimately connected with the conductivity of the salt. Amongst other explanations which have been put forward is the possibility that the increased gradient close to folds are relics of the much higher temperatures which must have been developed locally during, and as a result of, earth folding.

Actually the temperatures involved, even in the deepest wells and in those areas where the gradient is highest, are small in comparison with temperatures to which we are accustomed in the laboratory. For example, a temperature gradient of 1° F. for every 85 feet of depth would mean a temperature of the order of 200° F. at 10,000 feet, and there are not many places in the world where one would expect the temperature at 10,000 feet to exceed 280° F. From an engineering point of view such temperatures are not excessively high, and temperature gradients have been mentioned here at such length firstly because of their general interest and because variations in temperature gradient may later be more closely correlated with other geological conditions than have yet been found possible, and secondly because (as is well known) they have an important bearing on cementing operations, the setting times of cement being greatly shortened by increased temperatures. Thus a cement which has an initial setting point of 3¼ hours at a temperature of 100° F. will have an initial setting point of only 1¼ hours at a temperature of 150° F., and it follows that as the depth of cementation increases the type of cement used must be changed in the direction of obtaining slower and slower setting cement. It should also be noted that as temperatures become higher, the ease of penetration of water from mud into porous strata increases, and this point may possibly prove of importance in connection with sealing effects at great depths.

### (C) Increased Pressures.

We now come to by far the most important geological effect which has to be considered in relation to deep drilling—namely, the increase in pressure with depth—and we shall in the first place consider only the fluid pressure which manifests itself (for example) in the height to which water or oil rises in a well when a porous reservoir is penetrated.

If we fill a vessel with sand, and the pore spaces in the sand with water, the fluid pressure at any point in the vessel will simply be the hydrostatic head at that point. Generally speaking, we should expect the same to apply to all water-saturated sands which outcrop at the surface, and through which fluid movement can take place with reasonable ease, and in fact it is frequently (though not always) found that down to depths of, say, 3000 feet (in some places less and in some places more) the fluid pressure (whether of oil or water) encountered in any sand is equivalent to a corresponding hydrostatic head. Artesian wells generally form no exception to this rule, since in such cases the outcrop of the sand from which the water is being produced is at a higher level than that of the actual well, and there is no difficulty in applying a similar explanation to many of those oil wells which have flowed from moderate depths, the weight of the column of oil and gas

filling the tubing or casing in such a well being considerably less than the weight of a corresponding column of water.

If, as we reached greater and greater depths, the fluid pressure continued to increase only in accordance with the corresponding hydrostatic head, the problem of its control during drilling would be a comparatively simple one, since if a column of mud of any particular gravity 2000 feet long is sufficient to prevent exit of fluid from a sand the pressure of which is equivalent to a head of 2000 feet of water, a column of the same mud 8000 feet long will similarly prevent exit of fluid from sand the pressure of which is equivalent to a head of 8000 feet of water. Unfortunately what often happens is that, when we exceed a certain depth or range, we encounter fluid pressures in excess of the corresponding hydrostatic heads, sometimes rather more than twice as great. In other words, although in shallow wells fluid pressures do not normally exceed (very roughly) $\frac{1}{2}$ lb. per square inch for each foot of depth,* in deep wells fluid pressures of the order of 1 lb. per square inch for each foot of depth have been encountered, and it is these pressures in excess of hydrostatic heads which introduce what is undoubtedly the chief complication (additional to the problem of the very long transmisson shaft) in most deep-drilling work. For whereas with hydrostatic heads mud of normal weight can effectively control oil fluids in sands, the difficulty or impossibility of using mud of such weight as will control fluid pressures of double the corresponding hydrostatic heads has made necessary the introduction of those expensive mechanical devices which are included under the term "pressure equipment."

At least three explanations have been put forward for the occurrence of abnormally high pressures (by which are meant pressures greatly in excess of the corresponding hydrostatic head), but before considering these in detail, we should note that all of them have in common the assumption, which seems inescapable, that free fluid movement in the reservoir under consideration is in some way prevented or made very difficult, so that the high pressures, however applied, are prevented from being dissipated. Whether this absence of free movement is due to sealing near the outcrop or to permeability conditions in the porous rocks as a whole we do not know, but an explanation of the latter type is perhaps the more probable, and is analogous to that which (in Burma and India at least) we often have to invoke in order to explain the great reductions in pressure which take place even in shallow sands, without any appreciable advance of edge-water. This absence of free fluid movement is important not only because it prevents dissipation of very high pressures, but also because, if the effective size of the reservoir under consideration be small, and filled with water, the addition of comparatively little water would have the effect of raising fluid pressure rapidly. Conversely, and again considering only such a relatively incompressible fluid as water, it would seem to follow that the removal of comparatively little water from such a reservoir would cause a rapid lowering of pressure.

We shall have to refer to these points in more detail later, but for the present shall pass on to a consideration of the three most important theories

* We may assume that the water in question will usually contain some dissolved solids, and will therefore be heavier than fresh water.

which have been put forward to explain the actual development (as opposed to the preservation) of pressures greatly in excess of the corresponding hydrostatic heads. These are [2] :—

(*a*) That the pressures in excess of hydrostatic values are inherited or "fossil" pressures, preserved by sealing of outcrops from a time when the thickness of strata above the bed in question was much greater than it is now.

(*b*) That the pressures in excess of hydrostatic pressure are due to earth movement.

(*c*) That the pressures in excess of hydrostatic pressure are due to the fact that the effective weight exerted on the fluid in the reservoir in question is not the weight of fluid occupying the pore spaces, but the actual weight of superincumbent strata, which for convenience we may call the "earth pressure."

It is probably not much harder to account for the actual sealing of the reservoirs, however accomplished, on the first two than on the third theory; but this third theory—that of the actual dead-weight earth pressure—appears to the writer to have the following advantages over the other two :—

*First*, its very wide application, and its absence of dependence on any particular assumptions as to previous geological conditions;

*Second*, the fact that there is no reason to think that (for example) alternations of sandstone and shale at a depth of 6000 feet should be able to support, as does a girder in a building, the weight of material known to lie on top of them. On general considerations the probabilities are against an assumption of such very great strength as this down to very great depths, and we have practical demonstration that it is not so in some mining operations and, possibly, in the behaviour of what has been called "heaving shale," in some of our oil wells. This "heaving shale," as is well known, is in certain circumstances forced into our wells (in much the same way as would be a very plastic solid) under a pressure which can be shown to be in excess of hydrostatic, and which is in fact probably equivalent to the corresponding "earth pressure"*;

*Third*, the fact that, as first noted by Comins,[3] no instance is yet known where the fluid pressure encountered at any point in a well has been in excess of the calculated "earth pressure" at that point.† If either of the other two explanations—inherited pressure or pressure due to earth-folding—had a wide application, one would expect somewhere to encounter pressures in excess of "earth pressure."

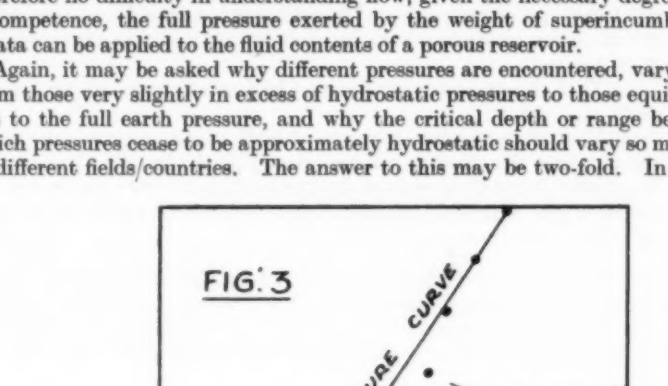
It may be asked how, on this theory, the earth pressure is transferred to the fluid in a porous sandstone (for we have no reason to think that the earth pressure would be great enough to crush individual sand grains, and thus to destroy or greatly reduce the porosity of a sandstone). The answer to this is presumably, as hinted above, that if a vessel is completely filled with a

* Note, however, that some (bentonite) shales expand on wetting, and that the effects noted may be, in some cases at least, directly due to this swelling.

† But see footnote on p. 386 below.

very slightly compressible fluid, such as water, an exceedingly slight increase in fluid will be sufficient to cause a very great increase in pressure. Such a small increase in fluid can easily be supposed to be squeezed out of a shale overlying or underlying a sandstone, and from this point of view there is therefore no difficulty in understanding how, given the necessary degree of incompetence, the full pressure exerted by the weight of superincumbent strata can be applied to the fluid contents of a porous reservoir.

Again, it may be asked why different pressures are encountered, varying from those very slightly in excess of hydrostatic pressures to those equivalent to the full earth pressure, and why the critical depth or range below which pressures cease to be approximately hydrostatic should vary so much in different fields/countries. The answer to this may be two-fold. In the




first place, all geologists are aware that different degrees of incompetence are exhibited by different strata. These differences are usually studied in terms of the reactions of the different strata to horizontal pressure, but it may be assumed that corresponding differences would appear in their reactions to vertical pressures. Also it may be that conditions similar to those indicated diagrammatically in Fig. 3 for a well drilled by the Burmah Oil Company, Limited (where pressures increased gradually from those roughly in accordance with the hydrostatic head to those equivalent to the corresponding earth pressure), occur more frequently than we have imagined, and that such conditions are due simply to the increasing effects of added loads on ranges of strata which have an approximately constant average degree of competence.

In the second place—and this is probably the more important point—it is certain that there will be differences in the extents to which porous

strata can be rendered relatively impervious to fluid movement. It is true that in general the possibilities of such sealing will increase with increasing depth, but apart altogether from the question of depth, one is much less likely to find sealing in a succession of coarse sandstones than in a succession of alternating shales and fine argillaceous sandstones, and fuller analysis of observed facts all over the world may later show that all gradations between reservoirs which at very great depths (say 8000 to 10,000 feet) exhibit only pressures approximating to the hydrostatic head, and those which at similar depths show pressures of rather more than twice this order, can be explained, largely at least, on the basis of relative permeabilities. This is a speculation which the writer has had no opportunity of verifying, and in partial support of it he can only mention that in Burma and India, where abnormally high pressures are common at great depths, the tendency for edge-water to advance as oil and gas are removed appears to be much less marked than it is in general in America, where pressures of the order of the corresponding earth pressure appear to be less frequently encountered. It may be, of course, that the apparent difference between conditions at great depths in Burma/India and in America will with fuller evidence disappear, and, in any case, we must avoid the incorrect assumption that the absence, at deep wells, of equipment for drilling under pressure is necessarily an indication that fluid pressures in such deep wells are equivalent to the hydrostatic head. Pressures of the order of, say, one and a half times the hydrostatic head can be controlled with reasonable ease by suitable mud, and would not normally necessitate drilling under surface pressure conditions. Where pressures of this order exist (and they may be very common in deep wells, *e.g.* Kettleman Hills) we must assume, according to the theory adopted above, that freedom of movement in the water reservoir, although restricted, is sufficiently great to prevent the full earth pressure from being transmitted to the fluid contents of the reservoir (in the same way as a leak in a bicycle pump will prevent the full pressure developed by the user from being transmitted to the reservoir being filled with air). In such cases, incidentally, we would not expect " bleeding " to be very valuable, the effective size of the reservoir being too great.

Lastly, short reference may be made to two points of possible practical importance which emerge from this study of the causes of high pressures in deep wells :—

(*a*) The possibility of reducing high pressures in water sands by bleeding off relatively small quantities of water.

(*b*) The possibility, in some deep wells, of calculating the maximum (and in some cases the probable) fluid pressures to be encountered at any given depth.

(a) *Possibility of Reducing High Pressures in Water Sands by Bleeding Off Relatively Small Quantities of Water.*

This possibility has already been referred to, and in spite of the rather poor chances of success and the obvious risks involved, it would seem wise to keep the possibility in mind, especially if and when we should be dealing with the problem of developing a proved oil sand below one or more " earth pressure " water sands. In such a case the lowering of pressure in the water

sands, if this were found possible, would do away with the necessity for high-pressure equipment methods in all wells drilled for ordinary development purposes. The amount of "bleeding" which would be necessary depends mainly on the effective size of the reservoir, and its permanent, or semi-permanent, effectiveness would depend on the rate, if appreciable, at which pressure when reduced could be built up again. Only actual experiment is likely to yield reliable information in these respects, but we may note, to get some idea of the order of the quantities involved, that pressure in a water reservoir the effective size of which is one million barrels would, theoretically (and postulating no rapid replacement), be reduced from an "earth pressure" of, say, 6000 lbs./in.$^2$ to the corresponding "hydrostatic pressure" of about 2600 lbs./in.$^2$ by bleeding off less than 10,000 barrels. The actual rate at which water could be removed by bleeding would, of course, depend mainly on the permeability.

(b) *Possibility, in Some Deep Wells, of Calculating the Maximum (and in some Cases the Probable) Fluid Pressures to be Encountered at any Given Depth.*

If we accept the view that abnormally high pressures in deep wells are due to transference of actual earth pressure to the fluid contents of sealed or partly sealed reservoirs, it follows that we can at once deduce the maximum fluid pressure which can be encountered at any depth, this being simply the corresponding "earth pressure" at that point.* We can now go a step further than this, and say that if in any well at any particular depth—say at 5000 feet—fluid pressures approximating to earth pressures are encountered, then (if strata of the same general type are expected) it may be taken as most probable that at great depths—say at 10,000 feet—fluid pressures approximating to earth pressure at this greater depth will be encountered. In other words, in such a well it is reasonable to use the earth pressure calculation as an indication not only of the *maximum* fluid pressure to be encountered, but also of the *probable* fluid pressure which will be met in some at least of the porous strata penetrated.*

If so, it follows that unless the mud column in use in a well as it becomes deeper and deeper is equivalent in weight to a corresponding column of earth, the "static" pressure control necessary at the surface must continuously increase. And even if the mud is of this weight, the total pressure required from the pumps to keep the mud in circulation must continuously increase. This presents a difficult drilling engineering problem which, in some regions, may impose rather severe restrictions on maximum drillable depths, and which deserves detailed advance consideration in respect of every pressure well in contemplation (at any rate, as soon as it appears likely to be desirable to drill beyond certain depths).

Prediction becomes more difficult if it is known that beyond a certain depth the whole nature of the strata will change, and that, as an example, a well exhibiting (at moderate depths) fluid pressures of "earth pressure" value will at greater depths pass from shales with subsidiary (and possibly

* A proviso is here necessary to the effect that the earth pressure might be applied to the reservoir in question some distance down dip from the point actually under consideration, in which case it is conceivable that pressures somewhat in excess of the true earth pressure at the point in question might be developed.

lens-like) sandstones into thick permeable sandstones. Even in such cases, however, it would seem wise to allow for the *possibility* that pressures up to corresponding earth pressures may be met with at greater depths.

The thanks of the writer are due to the Burmah Oil Company, Limited, for permission to present this paper.

*References.*

[1] "Problems of Petroleum Geology" (*American Association of Petroleum Geologists*, 1934). Part VII gives much useful information in respect of oilfield temperature gradients, and theories to account for these.

[2] Keep and Ward, "Drilling against High Rock Pressures with Particular Reference to Operations Conducted in the Khaur Field, Punjab," *J.I.P.T.*, 1934, **20**, 992–993, and discussion.

[3] Comius, *J.I.P.T.*, 1934, **20**, 722–725.

*DISCUSSION, at Yenangyaung, 28th August, 1936.*

MR. J. A. BUTLIN said that they had all listened to Mr. Abraham's paper with great interest, and he was sure that a number of those present would have questions to put. There were a few points which struck him, and with regard to temperature, it had been pointed out that sandstones are the best conductors of heat, also that temperatures rather follow the good conductor than go straight across the bedding planes. Another point made was that with higher temperatures the water in the circulating mud would go into porous formations more easily than from cold mud.

The effect of temperature on the initial set of cement was briefly touched upon, and he would like to point out that, so far as cement mixing was concerned, mixing with hot water gives a viscous mixture, but if cold water is used a good mix results. In other words, both as regards mud and cement the effect of temperature is to allow more free water. This was an important fact.

Another observed fact is that the temperature of mud coming out of a hole does not approach the bottom-hole temperature known to exist, and he put this down to the fact that the sides of the hole are coated with mud and this mud is an insulator. ing these facts into consideration, the effect of bottom-hole temperature on cementing will not be so great as one was led to suspect.

As regards the explanation for the high pressures met with, he would be inclined to think that the drop in pressure on removal of water might not take place as rapidly as suggested by Mr. Abraham. He had been in a number of mines, both coal and metal, and had noted the effect of crushing when roads are driven. It is a common sight to see steel beams bent and twisted and props broken. In Long Wall Face working at one time it was the custom to undercut the coal, and rely on the roof pressure to break the coal from the face. This suggested that as soon as support is removed, crushing takes place, and it had occurred to him that when the pressure is released by the well, the crushing observed in much harder and older rocks of the Carboniferous Age would take place in the softer Tertiary rocks to a much greater extent, and the pressures would be maintained for a considerable time in the rocks.

MR. C. E. KEEP said that referring to the presence of pressures greater than the equivalent hydrostatic head, the essential point, to his mind, was that the fluid must be "bottled up" and unable to obtain outlet at the surface. Granted this was so, several explanations of the cause of the high pressures were possible, although he was personally in favour of the theory that it was due to incompletely relieved folding stresses, at least in certain instances. When the paper on Khaur was read, the then President of the Institution, Mr. Dewhurst, put forward a fourth suggestion regarding the cause of the high pressures at Khaur—namely, that intrusion of water from below was an important factor.

He considered that it was an engineering problem to determine at what depth any particular sandstone stratum was incapable of supporting the weight of the superimposed beds, and therefore threw dead-weight earth pressure on to its fluid contents. He admitted that in the Punjab the known pressures at depths of 5000 feet were markedly similar to the equivalent earth pressure—namely, somewhat in excess of 5000 lb. per sq. in.

Referring to Fig. 3 illustrating the paper, he remarked that it was indicated that down to a certain depth the strata were capable of carrying the earth pressure, but at a certain considerably greater depth the full pressure was transmitted to the fluid.

Mr. E. J. Bradshaw said that he doubted whether, even at comparatively shallow depths, such poorly consolidated rocks as the Tertiaries at Yenangyaung would be competent to bear the weight of the superincumbent beds. Though "shells" were usually discontinuous, it was possible that they might be sufficiently competent to relieve lower beds of part of the load. In this connection he suggested that there was a possibility that structure might be of some importance, inasmuch as the lateral support derived from the arching effect of folded beds might increase considerably the resistance to crushing offered by beds which would otherwise be incompetent. There was evidence which suggested that in mining, the nature of the subsidence might be affected by the dip of the strata. The suggestion that structure, by producing an arching effect, might affect competency had only just occurred to him, and he had not given it any previous thought; it was a matter on which the views of engineers would be of interest.

Mr. J. Coates said that during the discussion on the origins of sub-surface pressure, it was mentioned that in some fields the pressure in an oil sand, although initially approximating to the corresponding hydrostatic pressure, was not maintained by the advance of edgewater when the oil was removed, as would be expected if communication were free between the sand and the origin of its pressure.

It was also mentioned that on any of the theories explaining the occurrence of abnormally high pressures (approximating to "Earth Pressures") in deep wells, it was postulated that the water in the sands was unable to move away freely through the sands.

He asked if the author of the paper had any information whether the development of abnormally high pressures commonly occurred in fields which also showed an absence of edgewater advance.

Mr. J. Bayliss said that a possibility occurred to him, although he did not know if actual conditions existed to justify it. While he could see the force of the theory as applied to liquids and plastic solids which are incompressible and would react in the same manner to a very small movement, as in the author's instance of the mercury in the container, it seemed to him that when dealing with gas pressures the position would be somewhat different. He asked whether it were not a fact that gas pressures are occasionally encountered which are of the order of the earth pressure? If that were the case, did the author think it possible for there to be sufficient earth movement to compress the gas to that extent.

Mr. C. E. Keep asked whether the author had any information regarding the development of abnormal pressures—that is, pressures greatly in excess of the equivalent hydrostatic head—in areas of really gentle folding, or were such pressures confined to areas of fairly severe, and relatively recent folding, such as one was accustomed to in the oilfields of Burma and India?

Mr. W. E. V. Abraham said, in reply to Mr. Coates, that he had not been able to trace any general relationship between regions in which very high fluid pressures occur and those in which the advance of edgewater tends to be slow or not observable. He had, however, referred to the point that in Burma and India, where high-pressure troubles at depth seemed to be relatively more frequent than in America, the advance of edgewater was as a rule slower than normally found in America. He suggested that a very fruitful line of research might be to collect deep pressure data from different parts of the world and to see whether any such general relationship exists. A similar remark would apply to the possible relationship suggested by Mr. Keep between age/intensity of folding and occurrences of abnormally high fluid pressures.

In reply to Mr. Bayliss, he agreed that the compressibility of gas, or even of an oil/gas mixture, was much greater than that of water, but he would not say that this completely ruled out the possibility, on the earth pressure theory, of very high pressures being encountered at depth in gas or oil sands. The question was one of degree.

He welcomed Mr. Butlin's first-hand evidence as to the existence of high pressures in coal-mines, a subject which he (Mr. Abraham) had not studied, but said that he had not envisaged pressures high enough to fracture or deform quartz grains. He agreed, however, that porosities of sandstones might in some cases be lowered by crushing of cementing material.

He agreed with Mr. Bradshaw and Mr. Keep that the whole subject of very high fluid pressures might with advantage be studied from an engineering point of view, taking into account actual rock strengths and structures.

*Written Discussion.*

MR. E. J. BRADSHAW, in a subsequent written contribution to the discussion, wrote that he was of opinion that more or less incoherent Tertiary rocks, such as those at Yenangyaung, were incompetent to support the weight of the superincumbent strata. The experience of mining engineers furnished ample evidence that in many cases even well-consolidated rocks were incompetent to bear the weight of the superincumbent strata for any great length of time. It might take months or years for the effect of underground subsidence to work its way up to the surface, as in the Chapin Mine of the Menominee iron range. In the copper mines of Lake Superior, where the beds are of a reasonably competent type, openings can usually be kept open indefinitely by leaving a few pillars, but even here it is found that when a depth of a mile is reached, the pillars are unable to withstand the pressure of the overlying rocks, and that they shear off with explosive violence, causing small earthquakes. There are many references to surface subsidence above shallow workings, and it seems likely that in such a field as Yenangyaung there exists no critical depth above which the strata are competent and below which they fail, but rather that every bed has to support the weight of the superincumbent strata.

If this be so, then some explanation must be sought for the persistence of hydrostatic pressures down to an apparently critical depth below which there is a sudden increase in the fluid pressures encountered during drilling, to an amount approximating to "earth pressures." Mr. Bradshaw agreed with Mr. Abraham that crux of the matter was the sealing of the strata containing the fluids. While it did not necessarily follow that because beds were subjected to compressive stress, the contained fluids should be in an equal state of compression, it was quite possible, where porous beds the voids of which were filled with fluids had been sealed and, possibly contemporaneously, had suffered compaction, that the load might be transferred to the fluid, and that in some cases the fluid itself might be supporting the whole weight of the superincumbent strata. In an interesting paper on surface subsidence at the Goose Creek oil and gas field, Snider* quotes from the views of Veatch† on the causes of tidal fluctuations in water wells, as follows: "In the case of water under artesian head (in a sand), its pressure against the cover tends to elevate it, thus placing the overlying clay under an upward stress. The addition of any weight at the surface tends to disturb the equilibrium. If there is no outlet, and if the weight is applied uniformly, the additional weight cannot change the position of any portion of the mass, except to the very slight degree of the elastic compressibility of the water and the soil. If, however, there is any escape for the confined water, such as would be afforded by a well tube, the mass will yield, and the water be forced up in the tube."

If it be agreed, first, that every bed is incompetent with respect to the load upon it, and secondly, that the fluid in any particular bed may, if it is unable to escape, be subjected to the load of the superincumbent strata, then the observed fact that down to a certain depth the pressure is hydrostatic, whereas beyond that depth it becomes "earth pressure," strongly suggests the explanation that beyond that critical depth the fluids were unable to escape either laterally along the bedding or vertically across the bedding planes to beds above or below that containing the fluid. Above the critical depth the excess fluid may have been able to escape, either vertically or laterally, when the containing beds were subjected to compaction, and, as a result, their pressures are the normal hydrostatic pressures usually encountered, or, alternatively, the degree of compaction may have been insufficient to reduce the porosity of the rocks sufficiently to transfer the load of the superincumbent strata to the contained fluids. If it happens, as appears to be the case, that at depth the pressures encountered, though greater than the hydrostatic pressure, do not increase uniformly with expected rock pressure, the explanation may depend partly on the extent to which different types of rock suffer reduction of porosity under load, and partly on the extent to which the permeability is reduced as a result of compression.

Finally, Mr. Bradshaw agreed with Mr. Butlin in doubting whether the "bleeding" of high-pressure sands would be an effective solution of the difficulty, since high pressures at depth appeared to be a result of the incompetence of the beds, and there were so many recorded instances of the persistence of subsidence over periods of years. Bleeding could only be successful if, on the release of the "excess" fluid, there were no further compaction of the rocks, whereas it seemed likely that removal of the contained fluid might, in many cases, lead to further compaction and subsidence, Snider‡ has

* Snider, L. C., "Surface Subsidence in the Goose Creek Oil and Gas Field, Texas," *Bull., A.A.P.G.*, Vol. XI, Pt. 2, 1927, pp. 729–745.

† Veatch, A. C., *U.S. Geol. Surv. Water Supply Paper*, No. 155, 1906, pp. 65–66.

‡ Snider, L. C., *loc. cit.*, p. 742.

suggested that such subsidence is common, and that the craters, commonly called "blow-outs," which sometimes occurred at high-pressure wells, were actually the surface indications of subsidence at depth caused by the formation of cavities due to the removal of sand and fluids from the producing strata.

MR. ABRAHAM, in reply to Mr. Bradshaw's written contribution, wrote :—

A sparrow alighting on the strongest girder will cause the girder to sag, and from this point of view it is quite true that, normally, each stratum bears the strain of the superincumbent load. But just as the bending of the girder under the weight of the sparrow is not readily detectable, so it is possible that down to a certain depth the weight of superincumbent strata does not deform sandstone or other reservoirs to the extent of allowing "earth pressures" to be transferred to the fluids which they contain. I therefore prefer to retain for the present the more general alternative types of explanation given in paras. 13 and 14 of my paper. At the same time, I appreciate the importance of the points of view put forward by Mr. Bradshaw, and suggest that these might provide material for a separate paper.

Mr. Bradshaw's views as to the poor prospects of improving conditions by "bleeding" are in substantial agreement with my own views.

# PREPARATION AND CONTROL OF MUD FLUID FOR PRESSURE DRILLING CONDITIONS.*

By Dr. J. T. Evans.

In discussing the preparation and treatment of muds for use in pressure drilling, it is proposed to consider only the use of loaded muds, and, in particular, muds loaded with barytes. At first sight it might seem that the installation of pressure equipment would remove the need for loaded muds; this, however, is by no means the case. Mr. Abraham has pointed out in a recent paper that the pressures to be dealt with at any particular depth may be equivalent to the weight of the overlying formations, *i.e.*, the pressure may be more than twice the hydrostatic pressure at the same depth. It is obvious that in dealing with such high pressures one cannot rely entirely on the pressure equipment available; it is impossible to use an ordinary 80–85 lb./cu. ft. clay or shale mud and apply a very high back pressure at the surface to control the well. In such circumstances a very heavy loaded mud must be used in conjunction with the pressure equipment. In other cases where the use of a loaded mud is not absolutely essential, it may be more convenient to use a loaded mud than an unloaded mud, *e.g.*, the pressure in a particular formation might be controlled equally well by say an 85-lb. shale mud with 500–600 lb. back pressure or, alternatively, by a loaded 100-lb. mud with a small back pressure of 100 lb. or so. The latter arrangement would seem preferable, because while the well was under only a nominal pressure, should another formation be encountered in which a higher pressure existed, it should be possible to control this immediately by increasing the back pressure applied at the surface.

## Preparation of Loaded Muds.

The preparation of a loaded mud consists essentially of two stages: (1) mixing clay or shale with water to give an ordinary rotary mud, and (2) mixing barytes with this clay/shale mud until the required weight is attained. If a supply of ground shale is available, both these operations are conveniently carried out using a funnel type mixer, such as is used for mixing cement. When clay is used, a paddle-mixer may be more suitable for the first stage. During either or both of these stages chemicals may be added to control the viscosity of the mud.

Before starting to mix any mud, one must decide which particular type of clay or shale is to be used as the base for the loaded mud, and also to what weight the clay/shale and water should be mixed before starting to load with barytes.

The answers to these questions will depend on the required characteristics of the final mud. Stability is always an important point in connection with drilling muds; the mud should separate as little water as possible, and

* Paper presented to the Burma Branch, Institution of Petroleum Technologists, at Yenangyaung, October 30th, 1936, and in London on May 4th, 1937.

should be capable of holding the barytes in suspension. While the barytes used consists of a very fine air-blown powder, most of which will pass a 300²-mesh, the specific gravity of this commercial barytes is generally 4·2–4·3, so that there is a considerable tendency for these particles to settle out despite their very small size. It is desirable, therefore, that the shale used for preparing the mud base should itself give a very stable suspension.

Now, in dealing with ordinary rotary muds, it is generally accepted that the most stable muds are those prepared from clays (or shales) containing a considerable proportion of particles of colloidal dimensions. The viscosity [1] of a mud is also mainly due to this colloidal material; coarser, inert material present in the mud, such as silt, sand, etc., contributes practically nothing to the viscosity until the ratio of solid : water becomes fairly high. Further, if the colloidal material is of what might be termed the " gel-forming " type, one would expect to obtain a fairly high viscosity for a low concentration of the solid in water. Aquagel is an example of material of this type; good naturally occurring clays contain varying percentages of such material, and the higher the percentage the lower the weight at which the mud becomes viscous.

It must be remembered that barytes is an expensive item; therefore the most economical method of preparing the loaded mud is to start loading from the highest practicable weight of shale mud. Hence, judged by the initial cost per barrel, the best type of shale to use is that shale which will give a stable, not too viscous mud at weights of 80 or 85 lb./cu. ft., or more if possible. The actual weight from which to start loading will depend on the final mud weight desired,[2] *e.g.*, for 100-lb. mud loading might start at 85 lb., whereas for 120-lb. mud it might be preferable to start loading from 80 lb. Although barytes is an inert material, and, as such, has comparatively little effect on viscosity, nevertheless it will take more than twice as much barytes to load from 85 to 120 lb. as from 85 to 100 lb., and consequently it will probably be more satisfactory to start with a somewhat lighter and less viscous shale mud.

The type of clay best suited as a base for a loaded mud may therefore be different from that suitable for ordinary drilling. For many normal purposes a stable 70–72-lb. mud of fairly low viscosity is quite satisfactory; should this mud become viscous at a slightly higher weight, it might be considered unsuitable for loading, on account of heavy expenditure involved on barytes. For example, the preparation of 900 barrels of 120-lb. mud representing 800 brls. for filling the hole, ditches, suction tanks and 100 brls. reserve, would require very approximately 135 tons of barytes if loaded from 85 lb., or 150 tons if loaded from 80 lb., or 165 tons if loaded from 75 lb. It may be mentioned that one barrel of 120-lb. mud loaded from 80 lb. contains approximately 240 lb. water, 160 lb. clay and 370 lb. barytes.

So far weight, viscosity and stability of the clay mud have been referred

[1] It is as well to mention here that, since this paper is not concerned primarily with viscosity and its measurement, the word " viscosity " has been used in a very loose sense, denoting an apparent viscosity as measured by one of the many arbitrary instruments in use. This is justified, since it is not proposed to discuss the influence of the various factors mentioned on " yield value " and " mobility " separately.

[2] There may also be the possibility that, at a later date, it may be desired to increase further the mud weight.

to briefly. Another characteristic to be considered is the reaction to chemicals commonly used to reduce viscosity. It is essential that the clay should react suitably with one or, preferably, more of these chemicals; in many, if not all, cases it will be necessary to add a reagent to the mud during the actual preparation to keep the viscosity within the desired limits. Many of the shales used for making mud in Burma react very satisfactorily with water-glass, and this is probably the chemical most commonly used for the control of viscosity.

If by adding water-glass to the shale mud the viscosity of the latter can be reduced, then obviously by adding water-glass and then more shale it is possible to obtain a heavier mud having a viscosity no higher than that of the original untreated mud. It might be suggested, therefore, that by using sufficient water-glass to give shale mud of the highest possible weight consistent with viscosity requirements, further economies in barytes could be achieved. It usually happens, however, that a very small percentage of water-glass gives the maximum viscosity reduction, and if this percentage is exceeded to an appreciable extent, the action may be reversed, and the effect will then be to thicken the mud. For reasons which will be given later, it is fairly certain that chemical treatment will be necessary very soon after the loaded mud has been put into circulation, and consequently it is not desirable to use too much of the chemical during the preparation of the mud. It is also unwise to use the highest possible weight of shale mud for loading (*i.e.*, highest possible weight obtainable through chemical treatment). The later history of the mud in circulation will in most cases show that the highest possible weight is not the optimum weight. Later evidence will explain these statements.

Before dismissing the subject of mud preparation and passing on to consider the performance of the mud in the hole, one other point may be mentioned, viz. that before any mud is mixed on a large scale, all the information possible should be obtained from small-scale laboratory experiments. This is a fairly obvious safeguard, but is nevertheless worth mentioning, as neglect of this precaution may involve considerable waste of both time and material. In bulk the mud is generally mixed in batches in a small tank of about 40 or 50 barrels, so that when laboratory tests are completed, the mixing of the first tank is important. This actually takes a considerable time, for the simple reason that the quantities of all materials used are carefully checked, as also weights and viscosities at the various stages of mixing. Having mixed one tank of mud to the required specifications, it is then possible, with the information thus available, to mix succeeding batches much more rapidly, making routine checks of the intermediate shale mud and the final loaded mud in every case.

### Conditions Affecting the Mud in Service.

When the mud is introduced into the hole and put into service, the conditions are very radically altered, and there are three obvious factors which may affect the characteristics of the mud. These are :—

(1) Pressure.
(2) Temperature.
(3) The shearing action of the beans.

*Pressure.* The maximum pressure to which the mud is subjected will depend on: (*a*) the specific gravity of the mud, (*b*) the depth of the hole and (*c*) the back pressure applied at the surface. With heavy muds having a specific gravity of 2 or thereabout, and an applied surface pressure of the order of 1000 lb./sq. in., the pressure exerted on the mud at the bottom of a hole some thousands of feet deep will amount to several thousand pounds per square inch.

Unfortunately, very little is known regarding the effect of high pressures on the viscosity characteristics of muds. Some experimental work has been carried out in America, the results leading the authors to conclude that pressure had little effect on viscosity. It seems essential, however, that many more experiments of this nature should be carried out, using various types of muds from different sources before any general conclusions can be reached. Meantime, the effect of high pressures on the properties of muds must be regarded as an unknown, but not necessarily negligible, quantity.

*Temperature.* It is well known that as wells are drilled deeper the formation temperatures tend to become higher, so that in deep wells it is to be expected that the temperature of the drilling mud will be appreciably raised. In three wells drilled in Burma to depths of 6000 feet or more, the temperature of the mud returns has been of the order of 120° F. It is probable that during circulation the temperature does not rise very much above 120° F., even when the mud is at the bottom of the hole, although a rise of say 10° or 15° F. may occur. In other words, during circulation at no point does the mud attain the actual temperature of the formations at the bottom of the hole. Rotary mud is not a good conductor of heat; moreover, as each formation is penetrated, it is plastered with a mud sheath which tends to act as a heat insulator. If the well should be shut down for a few days so that the mud is left undisturbed, then the mud at the bottom will tend to become hotter and approach nearer to actual formation temperatures. Under these conditions temperatures exceeding 150° F. have been registered in mud at about 6500 feet.

The effect of heating varies with different muds; in general, there is at first a decrease in viscosity with rise in temperature, followed by an increase in viscosity at higher temperatures. The minimum point on the viscosity temperature curve has been found at various temperatures by workers using different muds. Experiments on the effect of heating very heavy muds are rather complicated, on account of changes in weight which take place through evaporation; the loss of only a small volume of water from the mud will have a considerable effect on the viscosity. It seems probable that the effect of prolonged exposure of the mud to temperatures of 120° F. or greater will result in an increase both in viscosity and in the rate of gelation.

Another interesting temperature effect has been demonstrated as a result of recent experimental work in America. One very important requirement for a good rotary mud is its ability to seal off quickly the formations penetrated, allowing as little water as possible to permeate from the mud into the strata. The action may be regarded as analogous to filtration, water being expressed from the mud into the formation, leaving the mud solids in the form of a filter-cake or sheath on the sides of the hole. With a good mud

only a thin sheath is necessary to prevent further passage of water through this sheath and into the formation. With a mud of poor quality a much thicker sheath builds up, and more water passes into the formation. If the sheath is very thick, it is probably dislodged by the passage of the tools, and the filtering action proceeds indefinitely. The recent experiments referred to have indicated that as the temperature of the mud is raised, it becomes more difficult to obtain an impervious mud sheath, so that more water filters through into the formation; this applied to muds which were classed as good muds as well as to poor quality muds. Further reference will be made to this later.

*Shearing Action of the Beans.* While the well is drilling under pressure, the mud is returned from the hole to the atmosphere through the beans. In so doing it passes at considerable pressure and velocity through a very restricted opening The action here is to some extent reminiscent of the action of the so-called colloid mills used for preparing very intimate mixtures, emulsions, etc. Now, in an ordinary freshly prepared shale mud, made on a large scale from dry powdered shale, the shale particles are by no means completely hydrated. Passing such a mud through the beans tends to rupture the very small-shale particles exposing fresh surfaces, which then hydrate, attracting and binding a certain amount of water. As the amount of water bound on the shale increases, the amount of what may be termed "free" water decreases, and since this free water may be regarded as acting as a lubricant for the hydrated shale complexes, the viscosity of the mud as a whole increases. The stability of the mud is also improved, and the general effect may be regarded as an accelerated maturing of the mud.

It can be stated, as a matter of observation, that when a freshly prepared mud is introduced into a pressure well, the viscosity of the mud very soon increases—the change may be very rapid. Chemical treatment will be necessary, and it is advisable to start treating as soon as possible to prevent the mud from getting out of control. It has been mentioned earlier in this paper that in preparing the loaded mud it is inadvisable, in attempting to economize on barytes, to load a shale mud of excessive weight or to use too high a percentage of chemical. The greater the proportion of shale in the mud, the more pronounced will be the maturing action on placing the mud in service, and control by chemical means will not be facilitated if the mud is highly treated during preparation. If chemical control is impossible, the only method remaining is to cut back with water to a suitable viscosity, and then reload with barytes to the original weight. This is in effect equivalent to loading initially from a shale mud of lower weight.

### Admixture of Drilled-up Shales or Clays with Drilling Fluid.

It is quite certain that in many cases the admixture with the drilling mud of formations penetrated and drilled up may considerably modify the viscosity of the mud. Shales and clays vary greatly in their composition and in the nature and proportion of their replaceable or exchangeable bases. Any constituent from formations penetrated tending to react with exchangeable bases in the clay material of the drilling fluid would therefore be expected to modify the characteristics of the latter. For example, in drilling

through formations containing much gypsum or anhydrite, both of which possess a small solubility, one might expect reaction with a drilling mud made from a sodium-base clay or shale. Furthermore, in the case of mud fluid which is treated with soluble sodium salts to control viscosity, it is probable that reaction would occur with clays containing any appreciable amount of exchangeable calcium; if such reactions do occur, then in the case of treatment with water-glass one might expect the formation of small quantities of gelatinous calcium silicate in the mud, while at the same time the effect concentration of the sodium silicate would be correspondingly reduced. When first formed, the calcium silicate is gelatinous, but tends to pass to the crystalline state with time. In the gelatinous state the tendency would be to thicken the mud, but on standing and with crystallization the effect would be greatly decreased. This may partly explain the action of water-glass on mud from certain shales, the viscosity of which first increases on addition of water-glass, but then shows a reduction on standing, although the final viscosity may still be higher than the viscosity before treatment. Small-scale experiments show that certain muds can be made extremely viscous and unpumpable by adding chemicals which react with formation of calcium silicate, but these muds may thin down very considerably on standing.

## Chemicals Used for Reducing Viscosity of Muds.

Probably the best-known and most extensively used chemical is water-glass, a sodium silicate. Sodium carbonate, as commercial soda ash, has also found wide application. These chemicals have long been used for deflocculating or dispersing clays in the ceramic industry, and it is therefore natural that they were amongst the earliest chemicals used for the treatment of the clay suspensions used in rotary drilling. More recently various tannin materials have been used to a considerable extent, *e.g.*, the sodium tannate sold commercially as a boiler disencrustant, quebracho extract in conjunction with caustic soda, etc. In some cases tannin materials used alone, *i.e.*, without addition of alkali, have proved very successful.

Laboratory work has shown that extracts of various plant materials, wood, grasses, bamboo, etc., can be effective both in reducing the viscosity and in improving the stability of muds. Favourable results have been obtained in the laboratory with caustic soda, sodium carbonate and sodium sulphite extracts of such materials. Hence by-products from such industries as paper-making, when available near fields engaged in active drilling, may be useful for treating muds.

It may be mentioned here that a considerable number of theories have been put forward from time to time attempting to explain satisfactorily the deflocculating action of sodium silicate, carbonate, etc. Naturally the alkaline nature of these substances has resulted in considerable prominence being attached to the effect of the hydroxyl ion, and several theories attempt an explanation based on the action of the hydroxyl ion. Other writers consider that the deflocculating effect is due to the action of the sodium ion. So far no theory appears to have been generally accepted.

## Treating Mud in Circulation.

Before adding any chemicals to the well mud, it is advisable to ascertain the probable effect by making small-scale tests. These tests indicate the chemical or chemicals required and the percentage addition necessary to give the desired results. It is also important to know approximately the volume of mud in circulation and the time taken for the mud to make a circuit in the hole. With this information available, the quantity of chemicals required to treat the whole of the mud in circulation can be calculated. A solution is then prepared and added to the mud at a steady rate over the time for one or more complete circuits. To obtain the best results from the treatment arrangements should be made to ensure that the chemical is thoroughly incorporated in the mud. Any convenient device for giving good agitation may be rigged up.

It is found that the effect of the chemical treatment is evident for only a limited period; the viscosity of the mud gradually increases, and re-treatment becomes necessary. The period elapsing between successive treatments will depend on the nature of the mud, conditions in the hole, quantity and nature of chemicals added, etc. It may be as short as one or two days, and probably will not exceed a week.

After frequent additions of a small percentage of a certain chemical, it may happen that the mud eventually does not respond well to a further quantity of this chemical; the viscosity may show an increase instead of a decrease after treatment, or in other cases a slight "curdling" or "lumpiness" is noticed, which may disappear after very thorough agitation or after standing for a time, the mud then showing a reduced viscosity. At this stage it may be necessary, and is at least advisable, to resort to other treatment. In many cases by using another reagent quite satisfactory results can be obtained, again with further additions of the original chemical. Once again the importance of preliminary tests to indicate the correct combination and proportion of chemicals may be stressed. In certain cases it is quite possible to obtain entirely different results using the same quantities of two chemicals, but reversing the order of addition.

## Thixotropy.

Many muds exhibit the phenomenon of thixotropy to a greater or lesser degree; it is usually quite strongly evidenced in heavy muds after a period of service in pressure wells. Thixotropy is the name given to a particular type of reversible sol-gel transformation. In thixotropic bodies the transformation takes place without temperature change, whereas in the case of materials such as gelatine solutions the transformation from gel to sol is accomplished by heating, and the reverse change back to gel by cooling. By stirring a thixotropic gel, it is made fluid. If it is then allowed to stand without agitation, it again sets to a gel. Change of temperature is not necessary.

The thixotropic properties of mud are obviously of considerable importance. A moderate degree of thixotropy can be beneficial, assisting in retaining barytes in suspension. Also, if the mud gels lightly when circulation is stopped, it will hold all cuttings in suspension. This is a very desir-

able property in the case of fishing jobs, since it prevents sand, etc., settling around the fish. If the thixotropic properties of a mud become too strongly marked, it is apt to be rather a nuisance, the mud gelling very quickly and forming a gel of some strength. Hence, after a shutdown, pump pressures may be higher than usual when circulation is first re-started, although rotation of the pipe, if in the hole, or the movement of the pipe while being run in, should help to prevent the formation of a thixotropic gel or to break down the gel if formed. In connection with any operations requiring the running of instruments on a cable, the question of rate and strength of gel formation may be of considerable importance.

The ability to control the thixotropic properties of muds would be exceedingly useful, and it is possible that this can be achieved by chemical means. It has been possible to retard the rate of gelling of a thixotropic suspension of a pure substance by addition of small quantities of another chemical, but successful treatment of the more complex clay substances present in rotary mud may well be more difficult of approach.

## Sealing Properties of Very Heavy Loaded Muds.

It has already been mentioned that a good rotary mud will quickly seal off the formations penetrated, forming only a thin, but effective, filter cake on the walls of the hole. When drilling through shales which are liable to disintegrate and crumble when exposed to the action of water, or through bentonitic clays which tend to swell through absorption of water, it is obviously a matter of extreme importance that the mud should be capable of quickly forming a mud sheath which will not permit further infiltration of water from the mud to the strata.

In connection with the wall-building and sealing properties of muds, it has been stated that, when the filter cake contains 7 per cent. gel-forming colloidal material, it will prevent further loss of water from the mud. Thus it is claimed that a specially treated clay such as aquagel, containing a very high percentage of gel-type colloidal material, will quickly form a filter cake of the type necessary to prevent further loss of water, the filter cake formed being very thin. Ordinary drilling muds prepared from various natural clays and shales which in general contain very much lower percentages of gel-forming material than aquagel, take a correspondingly greater time to build up an impervious filter cake, and the cake itself is proportionately thicker. In the case of very poor muds, the cake may never be completely impervious.

Now, considering the case of very heavy loaded muds, *e.g.*, muds weighing from 120 to 150 lb./cu. ft., in the first place barytes constitutes by far the greater part of the total solid content of the mud. The remainder consists of clay or shale, of which again only a fraction (depending on the nature of the particular clay or shale used) will be colloidal material of the gel-forming type. It is obvious that for any particular clay/shale the higher the weight of the final loaded mud, the greater is the ratio of barytes to what may be regarded as the actual wall-building constituents. It may well be asked, therefore, whether very heavy loaded muds are normally capable of forming efficient mud sheaths and sealing the strata against penetration of water. Conditions are particularly severe, because with increase in temperature the difficulty of forming a good seal increases and, in general, these very

heavy muds are used at depths where the formation temperatures are high and the mud itself becomes appreciably heated.

It seems likely, therefore, that some of the troubles experienced with tight holes, crumbling and caving formations, etc., are the results of what may prove to be an inherent disadvantage of loaded muds. Supposing that the mud is capable of forming an impervious sheath, it seems fairly certain that this sheath will be of considerable thickness; hence, reaming to remove tightness, or the passage of the tools, will remove some of this sheath, and the filtering action will again commence. The question is of such extreme importance that it merits a detailed study.

*DISCUSSION, at Yenangyaung, 30th October, 1936.*

The Chairman, Mr. W. E. V. Abraham, in thanking Dr. Evans for his very interesting paper, emphasized that while weight *or* stability *or* pumpability was in itself easy to arrange, the difficult problem of the mud chemist was often how to arrange for all three simultaneously, and at reasonable cost.

Mr. J. A. Butlin asked what would be the effect of stepping down by stages to atmospheric pressure mud from a pressure well. He understood from the author's remarks that viscosity was increased by bringing the pressure down to atmospheric in one stage, and, as the viscosity question was such a big one, he wondered if in stepping down by 200-lb. stages to atmospheric pressure it would not have a beneficial effect.

A point about mud when fishing at the present time compared with a few years ago was that now if a fish was not recovered at the first attempt, it would not be stuck for the second attempt, while formerly a wash-over job invariably resulted when recovery failed at the first attempt. The sticking had a great deal to do with the quality of the mud, and apart from the straighter holes now being drilled, which make fishing easier, it gave an illustration of the difference as regards mud technique generally.

Viscosity and sand contents were checked daily on all ordinary drilling wells, and certain limits laid down for the drillers, with the result that fishing jobs presented no difficulties as regards sticking and the wear and tear on pumps was reduced to a minimum by the attention given to the elimination of the sand content in the muds.

It would be safe to say that the greater attention paid to mud and the co-operation of the chemist on this subject had made the task of the field technologist much lighter, and it was now a routine matter for the chemist to be consulted on all mud problems.

The results thus obtained had contributed to the faster drilling and fewer fishing troubles now prevalent.

Mr. J. Coates said that Dr. Evans, in describing the preparation of loaded muds, had referred particularly to barytes as the loading agent. He would be interested to know the reason for the almost exclusive use of barytes in practice, when there must be available other heavier substances suitable for loading, or, alternatively, other less heavy materials which could be used for the preliminary loading of a mud to give a heavy base for a final barytes loading.

Mr. C. E. Keep, in a written contribution to the discussion, said that one of the points that always appealed to him when the question of using heavy muds cropped up was the fact that aqueous suspensions of relatively poor stability were relied upon for drilling fluids. If the chemists could only develop a stable fluid of high specific gravity —say three times that of water—at a relatively low cost, all the difficulties of pressure control in the drilling of wells would be over. In fact, it might not even be necessary to circulate the fluid, as the rock cuttings would float to the surface, and the only remaining problem would be to conduct the heat developed by the boring action away from the bottom of the hole.

Failing any likelihood of such an ideal drilling fluid being developed, he would be interested to know whether Dr. Evans considered there were any possibilities in the use of a protective colloid for increasing the stability of loaded muds.

One of the difficulties experienced in deep drilling in many parts of the world was trouble with " heaving " shale. Such trouble was generally considered to be due to water expressed from the mud fluid contacting the shale formations, and thereafter

possibly causing expansion of the shale, if bentonitic,* encouraging slippage along bedding planes, or merely softening the shale and causing caving. He understood that certain work was proceeding on the use of water-in-oil emulsions † for drilling fluids, and would be glad to have Dr. Evans's opinion as to the suitability of such fluids for use in "heaving shale" territory.

Dr. J. T. Evans said that, in reply to Mr. Butlin, he considered it to be doubtful if stepping down pressure by 200 lb. stages, instead of reducing to atmospheric pressure in one stage, would be effective, since under these conditions the mud would pass through several beans in quite rapid succession, and although the pressure drop through each would be only 200 lb., the total effect would probably be similar to that of the one-stage pressure drop.

The reverse method of maturing might give the desired results, *i.e.*, to circulate the new mud for a period under 200 lb. back pressure, then under pressures rising by increments of, say, 200 lb.; in general, however, this was impossible, since conditions did not permit such a convenient arrangement.

In reply to Mr. Coates, he said that he had restricted himself to a consideration of barytes loaded muds, since barytes was the material generally used for loading mud for drilling operations in India and Burma, and on the field scale the author's experience had been confined to barytes loaded mud. Barytes could be readily obtained from a number of Indian sources, of satisfactory purity and specific gravity, and ground to the necessary degree of fineness. Samples of other materials available in Burma, *e.g.*, hæmatite, galena, zinc concentrates, had been examined in the laboratory for suitability for loading, but all proved unsatisfactory for various reasons. In particular, the samples received were generally not sufficiently fine, and settled out too readily. The cost of extra grinding to pass specification rendered these materials uneconomical by comparison with barytes.

In reply to Mr. Keep, Dr. Evans wrote :—

With regard to the first suggestion, it is interesting to note that a patent has recently been taken out in the U.S.A. covering a method whereby the hole is filled with a liquid having a greater specific gravity than the formation being drilled, *e.g.*, methylene iodide of sp. gr. 3·32 may be used.

The author's experiences with loaded mud suggest that when mud is mixed and introduced into the hole without an intervening period of storage in tanks/sumps, the mud becomes very stable, and has little tendency to settle barytes either in the hole (during shut-down periods or while making a round trip) or in the suction tanks. The thixotropic properties common to most matured loaded muds are chiefly responsible for this stability. If, however, it is desired to carry considerable stocks of loaded mud in storage, it seems very probable that the use of a protective colloid would be beneficial in retarding differential settling in the mud; the point is of considerable interest. At present the author prefers to hold only a small volume of mud in reserve, and to carry adequate stocks of raw materials and have an efficient mixing outfit capable of making mud quickly whenever desired.

The author has no practical experience of the use of water-in-oil emulsions for countering heaving shales. The idea is quite sound, since it has been observed on many occasions that shales which swell or disintegrate readily in contact with water are unaffected by contact with oil. It would seem, therefore, that a water-in-oil emulsion of sufficiently high specific gravity for the particular conditions should be useful in avoiding trouble when drilling through shales or clays of this nature. One aspect of the problem which would need attention would be the question of maintaining suitable viscosity with such emulsions, since it is to be expected that the reagents normally used would be ineffective.

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* W. E. V. Abraham: "Geological Aspects of Deep Drilling Problems." Paper presented to Burma Branch, 28th August, 1936.

† M. W. Strong: "Mud Fluids, with Special Reference to their Use in Limestone Fields," *Proc. World Petroleum Congress*, 1933, Vol. 1, p. 403, para. 8.

# DRILLING OF A DEEP PRESSURE TEST IN INDIA.*

By G. F. Wilson, B.Sc.

This note is written as an illustration of some of the problems which arise in the drilling of a well under pressure to great depth, in difficult formations, and of the means employed to overcome them.

Earlier wells by their failure at least showed the problems which would have to be met, and they make a formidable array. Briefly the troubles are :—

(*a*) A shallow zone of low-pressure sands which act as thief formations, causing loss of fluid and frequently complete loss of circulation.
(*b*) Deeper high-pressure water and gas sands.
(*c*) " Heaving Shale " formations.
(*d*) Hard formations which seriously retard drilling and tend to cause excessive deviation.

As an example of the peculiarities of the area we might quote an experience during abandoning operations of an earlier well. Within a space of 24 hours the well first took 1000 brls. of mud, and then, circulation having been regained, blew the drill-pipe out of the hole ! When plans were being made for this well, the difficulties listed above were catered for as follows :—

(*a*) By setting casing below the low-pressure zone.
(*b*) By drilling under pressure combined with the use of heavy mud.
(*c*) By continuous maintenance of pressure and by use of suitable treated muds.
(*d*) This was not capable of any direct solution, but by provision of a hydraulic table it was hoped that a straight hole could be maintained.

In addition, every care was taken to provide the best and most up-to-date equipment for the task ahead.

The history of the well is best dealt with in stages corresponding to the setting of each string of casing, of which there were six.

### *First Stage.*

This was to set a 24-inch conductor string at 450 ft. Even this small amount of drilling gave trouble, owing to difficulty in maintaining a straight hole.

### *Second Stage.*

The objective of this stage was to set 18⅝-inch casing below the low-pressure gas and water sands, at approximately 2000 ft. Apart from devia-

* Paper presented to the Burma Branch, Institution of Petroleum Technologists, at Chauk on November 27th, 1936, and in London on May 4th, 1937.

tion troubles, which were persistent and retarded progress materially, the main problem was to control the weight of mud; with an increase of only 1 or 2 lb. the formations took fluid rapidly; with a decrease of the same amount the well made water.

*Third Stage.*

The objective of this stage was to set 11¾-inch casing below the lowest horizon of the early wells, and it was expected that high-pressure water or gas sands would be met with, and that trouble with heaving formations might also be encountered. At the outset the well was drilled by normal methods, *i.e.* open hole with regular drill-pipe until the expected water sand was met with. Despite the fact that it was expected, this sand demonstrated the risks attendant on control of pressure by mud weight. The volume of mud to fill the hole was 1200 brls. approximately, and when the water was struck, despite all precautions mud weight started to fall, and it was only after 12 hours of strenuous work and much anxiety that the weight could be raised to a level sufficient to control the sand. A switch over to pressure drilling was made immediately, and drilling continued with constant maintenance of a surface pressure of 400 lb. per sq. inch.

Even this short stage of pressure drilling under a surface pressure of only 400 lb. per sq. inch showed very forcibly the necessity for duplication of lines and fittings if pressure was to be maintained continuously, and failure of fittings under the continued pressure was unpleasantly common.

Throughout this stage of drilling there had been no sign of heaving formations, but during the cementation of the 11¾-inch collar casing with 700 casks, which was carried out under atmospheric pressure using heavy mud, there was a tremendous increase in the amount of shale fragments in the returns, sufficiently large to cause grave anxiety. The cause of this sudden breakdown of the walls of the hole is obscure, but it demonstrated very clearly that the formations drilled through were dangerous, and that it was only the close control of pressure and use of good mud which prevented the well having to face the same conditions which caused the failure of the earlier holes.

During the shut-down opportunity was taken to make such improvements as experience of drilling under pressure had shown to be necessary. These changes included substitution of a hydraulic snubber for a wire-line snubber, duplication of mud lines and valves, substitution of 3000-lb. and 6000-lb. test valves and fittings for those of lower pressure, etc.

*Fourth Stage.*

Drilling was started in open hole, but using flush-joint drill-pipe and with the drilling packer in place, so that surface pressure could be applied immediately if necessary. It was not long before gas was met with, and the well had to be put under 500 lb. pressure. Later, further gas sands were encountered, which necessitated successive increases in well pressure up to 1350 lb. per sq. inch, mud weight being 80–85 lb. per sq. inch. Early in the stage an accident occurred which demonstrated the necessity, referred to above, for duplication of fittings. On one occasion, when starting in the hole, the master-gate valve jammed half open, so that the pipe could not

be run in the hole nor withdrawn without loss of pressure. By use of a locally devised gland on the spindle, it was possible to pull the clip back into the bonnet, run the drill on into the hole under pressure, load the mud to the required weight, and then remove the valve for repair without releasing pressure on the exposed gas-sands. In later stages two master-gate valves were fitted to avoid any such difficulty.

Drilling proceeded slowly owing to the hard formations and trouble with deviation. (It will be realized that pressure drilling precludes the use of many of the normal straight-hole drilling practices such as the use of long oversize drill-collars.) A good footage in an eight-hour tour was 8 ft., and with such slow progress the hydraulic rotary table effectively demonstrated its value. The ease and delicacy of control are such that it is an invaluable aid in drilling tough, steeply dipping formations and undoubtedly to its use is attributable the relative straightness of the hole.

Although progress was slow, it was steady, but after only 90 days of drilling there was a sudden loss of fluid in the hole and pressure built up *behind* the 11¾-inch string, indicating clearly that the casing was holed. Despite this, drilling was continued for a further 90 days, when there was a recurrence of the trouble in an aggravated form, and although the loss of fluid was checked by thickening the mud with Aquagel, it was decided that further drilling would be foolhardy and a string of 8⅝ inch flush-joint casing was run and cemented under a pressure of 600 lb. with complete success.

Most of the drilling in this stage had been through hard shales and mudstone, but one zone of treacherous formation was encountered where the walls sloughed in badly when first drilled through. By an increase in well-pressure and treatment of the mud with sodium tannate, this "heaving" was completely cured, and did not recur until the time of the 8⅝-inch casing cementation, where, as during the 11¾-inch cementation, there was a marked and embarrassing increase in shale in the mud returns.

Thus far in the history of the well the preparations made to guard against troubles—pressure drilling and mud control—had proved very successful, and the formations and troubles which had caused the loss of the earlier wells had been overcome without real difficulty. An ominous feature, however, was the speed with which the casing was holed and the evidence that there was communication with low-pressure sands through these holes.

Also, it was clear from the record of the rock pressures of the gas sands so far encountered that the rate of increase of pressure with depth was in excess of the increment of hydrostatic pressure, and that therefore one could not expect, even by the cementing off of the upper gas sands, that a reversion to open-hole drilling with light mud would be possible.

### *Fifth Stage.*

Despite the unfavourable factors mentioned above, the position after cementing the 8⅝-inch appeared excellent. The experience gained had shown that formations which had caused earlier failures could be overcome with ease, and that continuous drilling under pressure even for months was quite feasible. Unfortunately this optimistic outlook was soon discounted. Soon after the start of drilling, which was in open hole with 80–85 lb. mud, troubles with what is best described as sticky hole were encountered, *i.e.*

bits pulled tight when coming out of the hole and bridges were found when running in. There were no signs of pronounced caving, such as are usually associated with heaving shale, but conditions were definitely dangerous. Various attempts were made to ameliorate conditions, such as increase in well pressure, discarding oversize drill-collars, treatment of mud with reagents such as sodium tannate and aquagel, but all, with remarkable and disappointing uniformity, failed to improve conditions. Progress, however, continued despite the difficulties, but after making 400 ft. of hole, the pipe froze and circulation was lost. Some gas sands had been met which necessitated maintenance of well pressure, so that the fishing job presented an unusual problem. Complete recovery of the fish under pressure was possible only by cutting and pulling in 90-ft. lengths, and, in view of the time this would take, it was not favoured. Finally it was decided that to cut the pipe by explosive close to the bit, pump in heavy mud, and proceed by usual methods offered the best chance of success. No suitable shooting equipment was available in India, and the small internal diameter of the tool-joints limited the diameter of the shot, but finally, after considerable experiment, a shell of gun-cotton was fired in the drill-collars. Unfortunately this shot failed to cut the drill-collar, although, as later events proved, it failed by only a narrow margin. Following this failure it was decided to run the risk of a temporary loss of pressure and to try backing-off. This was done, the hole being loaded with very heavy mud after each back-off. Having reached the shoe, the mud weight was sufficiently high to balance the gas pressures, and maintenance of well pressure was no longer necessary. By washing over and cutting or backing off, the complete fish was recovered.

Soon after the resumption of drilling a strong gas horizon was encountered, which proved to have the remarkable rock pressure of almost 6700 lb. per sq. inch. The presence of this gas complicated the situation very seriously, since to control it called for maintenance of high mud weight and high well pressure—a common combination being 1500 lb. well pressure with 135 lb. mud. With such heavy muds friction pressures are of course higher than with normal light muds, and this, combined with the well pressure, resulted in a heavy load on the pumps, and a consequent reduction in rate of circulation—an undesirable feature in a hole where sticky conditions are prevalent. A further difficulty was that the high pressure and heavy barytes mud prevented successful use of the closed circulation system which earlier had proved of great value in reducing the pump load and increasing circulation volumes.

The sticky conditions continued to be unpleasantly conspicuous, there being few round trips during pulling it was not necessary to drill *up*. In this respect the hydraulic table proved of tremendous value, and it is very doubtful if any progress could have been made without its use. Various efforts, mainly directed towards effecting improvements in the mud, were tried, but again without success—or, more accurately, without lasting success, as some of the experiments gave temporary improvement. However, it was not long before the drill-pipe was again stuck. On this occasion fishing operations were only partly successful, and after sticking 6⅝-inch wash pipe, a whipstock was set and the balance of the fish side-tracked. Just before this fishing job a sudden but brief loss of mud had indicated that the 8¾ inch was holed, and that mud was being lost into shallow low-pressure

sands. Despite this, it was decided to attempt to drill out of the dangerous formations into harder and less dangerous beds before cementing. Very little more progress was made, however, before the pipe again froze, although on this occasion circulation was not lost. Circulation of an oil-mud was therefore tried, but failed, and later attempts at shooting were made, but also without success.

When fishing started it was found that the 8⅝-inch had collapsed and held the drill-pipe, and this complication to an already complicated job caused much delay. However, by careful milling with plain joints, the collapsed casing was swedged out, and recovery of the drill-pipe continued until it was found impossible to get wash-pipe over the top of the fish, and side-tracking was again necessary. During this fishing job a great deal of the washing-over and cutting was done under pressure, a feat which at that time was probably unique in the history of drilling. During the periods when surface pressure was not being maintained continously the gas was controlled by heavy mud, weights as high as 165 lb. per cu. ft. being used occasionally and 155-lb. muds being in common use.

At this point it was decided that there had been sufficient excitement for one stage of drilling, and 6⅝ inch flush-joint casing was run under 1500 lb. pressure, but, unfortunately, the string held up 1000 ft. from bottom. The casing was therefore pulled and the hole reamed with a Reed Reamer. Having pulled back into the shoe to string 10 lines, it was found that the 8⅝-inch casing had again collapsed, and the drill-pipe was frozen, a culminating piece of bad luck after a year of little good fortune. Once again, however, by milling and swedging, the collapsed casing was worked out and the fish recovered. Having again conditioned the hole, 6⅝-inch flush-joint casing was run under 1750 lb. pressure, but held up as on the previous attempt, and was cemented—thus terminating a drilling stage which had lasted a year and a half with over 300 days engaged in fishing operations.

### *Sixth Stage.*

At the beginning of the sixth stage the position was that 6⅝-inch casing was cemented just below a very high-pressure gas with 1000 ft. of open hole below and with two side-tracked fish running below the casing shoe. This was not an encouraging start, especially since in the open hole treacherous formations were exposed. On account of the danger of the gas breaking in around the shoe, the well was kept under pressure from the outset. This was more than a safety precaution, since tests after the cementation had revealed the presence of an unsuspected water sand somewhere in the open hole. After the start of drilling it was soon clear that the rate of circulation with two compound pumps was insufficient to keep the hole clear, and three-stage pumping was employed. The drill-pipe in use was 3½-inch externally flush with tool-joints of smaller internal diameter than A.P.I. pipe, and this, combined with the "friction pressure" of the heavy mud and the well-head pressure, raised pump pressures to 3200–3500 lb. per sq. inch. In spite of these exceptionally high pressures, drilling continued for three months without a serious breakdown.

Despite the difficult conditions, good progress was made, and 1000 ft. of hole were drilled in 2½ months—fair footage, considering the depth, the

hard formation, high well pressures and high pump pressures. Unfortunately, at this point the drill-pipe stuck when running in, and during fishing operations the shoe-joint of the 6⅝-inch was found to have collapsed. The loss of an overshot, and later the breaking of a die-collar just inside the shoe, necessitated prolonged milling inside the shoe-joint, which eventually windowed the casing. These minor fish were recovered, but when fishing started in the open hole, great trouble was experienced with the damaged shoe-joint and caving below the shoe. The fish itself was found to be binding with the old side-tracked fish left from the previous stage, and after the fishing string had been stuck four times within a week, although fortunately only temporarily, it was decided that the prospects of clearing the hole were negligible, and the well was abandoned.

Reviewing the history of the well as a whole the following points emerge :

(*a*) Pressure drilling for prolonged periods, and even fishing under pressure, are perfectly practicable, but call for the most careful rigging up to guard against temporary breakdowns, and also call for the very best equipment obtainable.

(*b*) In regions where formations are hard and footage rates low, the most serious objection to pressure drilling is the speed with which casing strings are windowed.

(*c*) Where rock pressures are known and can be handled by mud, it is probably best to regard pressure drilling as a stand-by, and not as a normal method of drilling. In the early stages of its development pressure drilling was regarded as a substitute for mud control; later they were regarded more accurately as complementary. Now I would suggest that in areas where progress is necessarily slow pressure drilling should be taken as an emergency control, more in the light of a blow-out preventer than as a method of drilling.

(*d*) The objection to the use of heavy mud is generally on the grounds of expense and difficulty of maintenance of weight, but experience in this particular well suggested that the increased fuel cost and equipment costs caused by drilling under pressure more than offset the cost of mud-loading materials. So far as maintenance of mud weight is concerned, it was found easy to keep weight at 145 lb. per cu. ft. for prolonged periods, and for emergencies such as occurred during fishing jobs muds weighing as high as 165 lb. per cu. ft. were made up.

(*e*) If heavy muds are to be used in place of light mud with well pressure, casing sizes, and hence drill-pipe sizes, require careful consideration from the point of view of pump pressures. At this well it was found that heavy mud doubled the pump pressure as against light mud. This was not due to the heavy muds being "thick." To the eye they appeared as thin as a good 85-lb. mud, but laboratory measurements showed that they were characterized by a high yield value and very low mobility. The modern tendency is towards full-hole tool-joints, but the use of external flush-joint pipe involves even smaller tool-joint openings than with A.P.I. standards. This is of great importance in deep holes and with small drill-pipe such as 3½-inch.

*Equipment.*

Although this note has designedly avoided references to the equipment, the following list may be of interest.

*Boilers.*

6, later 8—200 lb., 55 H.P.

*Pumps.*

4, later 6—$14\frac{1}{4} \times 7\frac{1}{4} \times 18$ inch.

4 { 2—4000 lb. per sq. in.,
  2—5500 lb. per sq. in. High test pressure water ends.

*Hoses.*

3 inch and $2\frac{1}{2}$-inch Champion-Barber steel hose.

*Engine, draw-works, and rotary table.*

$12 \times 12$-inch twin cylinder Ideal Ajaz B.N. Type draw-works.
Hydril Hydraulic rotary.

*Drill-pipe* (pressure stages).

$6\frac{5}{8}$ inch, $5\frac{9}{16}$ inch, $4\frac{1}{2}$ inch, and $3\frac{1}{2}$ inch Hydril external flush joint.

*Valves*, etc.

3000 lb. and 6000 lb. test pressures. The gate valves gave great trouble with cutting out when using barytes mud, and there was a tendency towards replacement of them by lubricated stopcocks.

# NOTES ON DEEP WELLS DRILLED IN IRAN.

By G. W. Colvill.*

The Anglo-Iranian Oil Company has since 1931 drilled four wells in Iran which may be said to come into the category of very deep wells. They are the following :—

(1) Yamaha No. 2; depth 8960 ft. (3) Pirgah No. 2; depth 10,025 ft.
(2) Qishm No. 3; depth 8294 ft. (4) Zeloi No. 4; depth 11,190 ft.

Of the first two mentioned, Yamaha No. 2 is notable only because it was drilled in 1931 by electrical power, and was then believed to be the deepest well in the world drilled by this type of power; also this well when completed carried 6333 ft. of open hole. Qishm No. 3 was drilled in 1935, and is notable because, owing to H.P. water shows encountered, it was necessary to use pressure drilling for the last 5300 ft. drilled. With 1·6 sp. gr. mud in circulation, a back pressure ranging from 600 lb. per sq. in. to 1100 lb. per sq. in. was carried when drilling and when running casing.

These notes will deal only with the last two wells given above, as they can both be included in a list of the deepest wells in the world; the last well mentioned, which drilled to 11,190 ft., in the ten deepest.

Our experience of deep-hole drilling has led us to believe that, provided the surface equipment is adequate, there are no particular problems to be faced owing to depth for present-day depths of up to 12,000 ft. The actual drilling has, if anything, become easier, and any problems that have arisen have been applicable to much shallower wells. Both Pirgah No. 2 and Zeloi No. 4 have been drilled without a fishing job or hold-up of any kind due to mechanical difficulties.

These wells were drilled with the same equipment, which was transferred from one to the other, and some details of this will no doubt be of interest :—

| | |
|---|---|
| Crown Block | Roller-bearing 36-in. sheave double deck. |
| Derrick | 136 ft. × 26 in. base, combination, steel. |
| Draw-works | Three-shaft, four-speed unit type with 26-in. dia. drum, 9-in. drum-shaft, line-shaft and jack-shaft. The draw-works are fitted with a 36-in. hydromatic brake which has been found to be an invaluable piece of equipment below 6000 ft. |
| Engine | 12 in. × 12 in. roller-bearing twin-cylinder working on 250 lb. per sq. in. steam pressure. |
| Pumps | 2 14 in. × 6¾ in. × 14 in. Duplex steam pumps with a working pressure of 2000 lb. per sq. in.<br>1 12 in. × 6¾ in. × 14 in. Duplex steam pump with a working pressure of 1000 lb. per sq. in. |
| Boilers | 4 81-H.P. locomotive type working pressure 250 lb. per sq. in. and with incorporated superheaters to give 50° of superheat. |
| Feed Pumps | 2 7½ in. × 4½ in. × 10 in. Duplex steam pumps. |
| Lighting Sets | 1 7-K.W. turbo generator. |
| Travelling Blocks | 66-in. 5-sheave roller bearing. |

* Anglo-Iranian Oil Company.

| | |
|---|---|
| Hook | 9-in. Wigle type. |
| Casing Elevators and Links | Side-door slip grip. |
| Rotary Table | 27½-in. fully enclosed type. |
| Tongs | Two-step type. |
| Slips | "Mission." |
| Casing Spiders | "Butler." |
| Swivels | 6-in. 150-ton and 100-ton, the latter used on the 3½-in. kelly. |
| Hoses | Rubber 5000 lb. per sq. in. type. |
| Drill Pipe | 6⅝-in. A.P.I. 25·2 lb. per foot Internal Upset Grade D.<br>4½-in. A.P.I. 16·6 lb. per foot Internal Upset Grade D.<br>3½-in. A.P.I. 13·3 lb. per foot Internal Upset Grade D.<br>3½-in. External Flush-Joint 13·3 lb. per foot Grade D, with 2⅞-in. A.P.I. tool-joint thread. |
| Tool Joints | A.P.I. full hole. |
| Weigh Indicator | "Martin Decker" Quintuplex. |
| Drill Collars | 3 30-ft.-long A.P.I. drill collars of the nominal size of the drilling string were used on each size of drill pipe. |

A standard cable-tool rig was also installed to act as an emergency hoist, and in order that the sand reel would be available for running acid-bottle inclinometers, etc.

We give below a brief history of each well as regards sizes of hole drilled and casing run.

*Pirgah No. 2.*

(1) 17½-in. hole drilled to 864 ft. with 6⅝-in. drill pipe, 15½ in.-71 lb. inserted joint casing cemented at 860 ft.
(2) 14¾-in. hole drilled to 3890 ft. with 6⅝-in. drill pipe, 11¾ in.-59 lb. inserted joint casing cemented at 3885 ft.
(3) 10¾-in. hole drilled to 5540 ft. with 6⅝-in. drill pipe, 8¾ in.-39 lb. inserted joint casing cemented at 5534 ft.
(4) 7⅞-in. hole drilled to 8130 ft. with 4½-in. drill pipe, 6¼ in.-24 lb. inserted joint casing cemented at 8022 ft.
(5) 5¾-in. hole drilled to 10,025 ft. with a composite string of 3½-in. A.P.I. and 3½-in. flush-joint drill pipe, the flush joint being used in the open hole.

*Zeloi No. 4.*

(1) 14¾-in. hole drilled with 6⅝-in. drill pipe to 3532 ft., 11¾ in.-59 lb. inserted joint casing cemented at 3528 ft.
(2) 10¾-in. hole drilled to 6004 ft. with 6⅝-in. drill pipe, 8¾ in.-39 lb. inserted joint casing cemented at 5986 ft.
(3) 7⅞-in. hole drilled to 9504 ft. with 4½-in. drill pipe, 6¼ in.-24 lb. inserted joint casing liner cemented from 5942 ft. to 9500 ft.
(4) 5¾-in. hole drilled to 10,873 ft. with a composite string of 3½-in. A.P.I. and 3½-in. flush-joint drill pipe, the flush joint being in the open hole.
(5) A liner of 4½ in. 11 lb. inserted joint casing has been cemented from 9300 ft. to 10,675 ft., the well will drill ahead using a composite string of 3½-in. A.P.I. and 2⅞-in. flush-joint drill pipe, the 2⅞-in. flush joint being used from the top of the 4½-in. liner downwards.

These two wells, although in the same locality, presented quite different drilling problems. Pirgah No. 2 met with heaving shale formations below 6000 ft., and this necessitated the use of a mud of as high as 1·95 sp. gr. to control the movement of these formations. The mud was made up from a 1·3 sp. gr. brine shale base with barytes added to bring up to the required gravity; as this mud picked up shale and became too viscous during drilling, magnesium chloride was added to bring the viscosity down to a reasonable working point. Pumping pressures of the order of 2600 lb. per sq. in. were necessary when the small size of drill pipe was in use. Zeloi No. 4 did not

meet with any troublesome formations until a depth of 9700 ft. was reached, and 1·42 sp. gr. brine shale mud was used down to that point; from there onwards a mud of 1·55 sp. gr. has been used, and the hole has stood up well. These two wells have been drilled from top to bottom entirely with rock bits in anhydrites, shales, salt, and some limestone, Pirgah No. 2 taking 10 months for completion and Zeloi No. 4 10 months to the present depth of 11,190 ft.

All casing strings were run with a float collar and cemented by the single-plug method. The rig-pumps were used to mix and place the cement, and no difficulties either due to temperatures or pressures were encountered in delivering as much as 1500 cu. ft. of 1·8 sp. gr. cement slurry at 6000 ft. The two deepest cementing operations were carried out at 9500 ft. and 10,675 ft., where the 6½-in. and 4½-in. liners were cemented; both operations were completed in about 70 mins. without any abnormal pressures being necessary to place the cement in position.

The deviation of the holes was measured every 250 ft. by means of an acid-bottle inclinometer run on a half-inch sand line from the standard rig. Both wells were kept within a limit of 5° with great ease, except when drilling in some extremely disturbed anhydrites and shales between 6200 ft. and 6700 ft. on Zeloi No. 4. It was necessary to plug back with cement from 6700 ft. to 6300 ft. on two occasions, but apart from the delay caused, the straightening operation proved to be fairly simple using a weight of less 200 lb. per inch dia. of bit with table revolutions of around 100 R.P.M., and using one reamer immediately above the bit with a second 60 ft. higher; drill collars between them and one drill collar above the top reamer.

It has been the practice not to load the block lines higher than with a factor of safety of 5 on the new line breaking strain. One-inch-dia. lines were used when drilling. Adhering to this loading necessitated stringing ten lines at various depths, according to the size of drill pipe in use. With the modern four-speed draw-works a multiplication of lines is no great disadvantage as regards speed, and besides ensuring against a failure, has been found to pay as regards the service obtained from the lines. This will be seen from the fact that only three lines were used on Pirgah No. 2, and Zeloi No. 4 is now only using its fourth. For running casing, a 1¼-in.-dia. line was used, and was kept aside specially for this work.

The average time for pulling out from 10,000 ft. was 4 hours. The drill pipe was at all times below 5000 ft. fitted with two non-return valves—one in the drill collars and one about midway in the string. These are used principally as an insurance against a blowout, and as the wells were drilled in unknown territory, were considered essential, even though they necessitated the filling of each stand of drill pipe with mud when running in, with consequent loss of time. It has been proved that each stand must be filled when running in, otherwise the mud becomes badly air-cut. The filling is done from a hose as the top of each stand is in the table.

The maximum footage drilled in any one day was 256 ft., but below 8000 ft. the best footage was about 160 ft., with a good average day being 80 ft. Below 10,000 ft. the best day's work was 100 ft., the average being about 50 ft.

The average life per bit below 8000 ft. was 120 ft. and it was usual to pull the bit after 40 hours on bottom irrespective of the formation being drilled,

the governing factor in the life of the bits usually being the wear on the roller-bearings and bearing-pins. There is a noticeable lag in the weight indicator and other instruments when working at depth, and it is advisable not to change members of the crew on such wells, as there is no doubt that "feel" for depth is developed and the knowledge of the hole is invaluable. The weight carried on the bits was at all times limited to about 1000 lb. per in. of diameter, and, as stated previously, the holes have been kept reasonably straight, although the formation drilled was steeply bedded.

The cellars on these wells were 16 ft. square by 10 ft. deep, with two open sides and with a sub-cellar 11 ft. square by 6 ft. deep sunk in the floor of the main cellar. The derrick is mounted on 17-in-dia. pipe piers, three of which are 6 ft. long and one 16 ft. long. Three of these are flanged to concrete blocks built into the main cellar walls, and the fourth is flanged to a concrete block at main-cellar floor-level. The effective depth of cellar below the derrick sills is therefore 22 ft., and allows ample room for our wellheads, which consist of two master gate-valves, a mud cross with various side lines, a gate-type blowout preventer, a mud cross from which the mud returns are normally taken, and finally an hydraulic type blowout preventer. All strings of casing are cemented to surface and flanged together (if they extend to surface), and all valves, etc., are fitted with remote controls.

The work done on these two wells was well within the capacity of the equipment, and there were no delays of any note due to mechanical breakdown.

# DEEP WELL DRILLING.

## DISCUSSION BY ROUMANIAN BRANCH.

A GENERAL discussion on the problems of Deep Well Drilling was held at a meeting of the Roumanian Branch at Ploesti on 27th November, 1936. The discussion was opened by Mr. G. ELIAS, B.Sc. (Member).

MR. ELIAS said: For the purpose of this discussion it is probably unnecessary to specify exactly when a well is considered deep, especially as the knowledge which has been obtained in drilling deep wells has, to some extent, revised our ideas of drilling shallow wells.

Inasmuch as suitable equipment is now obtainable, and as sufficient deep wells have been drilled in the world to give us considerable knowledge of the technique required, the possibility whether a deep well can or cannot be drilled does not arise. The problems we now have in drilling deep wells are two: firstly, the possibility of being able to complete them faster, and secondly, the possibility of being able to reduce the cost of such wells. The latter is a particularly important question when we consider that the deeper sands do not necessarily appear to be more prolific than the shallower sands, and if in some cases they do appear so, we have to consider whether it is not due to improved production methods and conservation measures.

In order to complete wells in minimum time and at minimum costs, the first necessity is to avoid accidents. Accidents will occur from time to time, but in the short time available for opening this discussion it is not intended to deal with this question.

To minimize the risk of accidents the obvious steps are to select suitable equipment, drillers and crews. The next precaution in order of importance is to keep the hole in good condition from spudding-in to completion. Here the all-important question of mud comes into play, and the condition of the mud plays many rôles in the drilling of a deep well.

One of the first problems to appear in deep drilling was the freezing of drill-pipe, and it is now known that poor mud conditions are usually the cause of this once-prevalent difficulty. To avoid freezing drill-pipe and casing, the mud must be kept comparatively free of suspensoids, this being best effected by: (1) Rapid circulation, (2) Maintaining sufficient viscosity, (3) Using vibrating screens, (4) Adequate settling arrangements, and (5) Control over the rate of thinning-up. Incidentally, in paying attention to these factors you will reduce pump wear (pump replacements being an important item in your drilling costs); also the cutting out of drill-pipe and tool-joint threads and the flush-holes of bits. It is surprising how many bits have to be discarded because the flush-holes have been cut-out beyond repair.

Both in America and in Roumania one finds examples of shales which are very sensitive to the characteristics of the mud used in drilling through them and after they have been drilled through. Such shales are usually called, rightly or wrongly, heaving shales. In fact, this term is almost universally

applied to shales which torment the driller. The problem offered by this type of shale has not been solved in every case, but undoubtedly the primary step is to keep down the amount of free water in the mud.

Very recently I had an example of the importance of maintaining the colloidal properties of mud. At a certain well no particular trouble was found in passing through a heaving shale, but a salt-bearing formation was encountered at greater depth. The salt spoiled the mud, and immediately trouble with the heaving shale ensued.

Once the characteristics of the formation in a new area have been established, rules for the conditioning of the mud can be laid down. The driller and his crew are usually able to carry out the necessary frequent tests and correct for deviation from proper conditions. The tests usually required are for weight, viscosity and free water.

It is probable that in the known fields here the finer tests, such as for $p_H$ value, viscosity by Stormer viscosimeter, etc., and the addition of chemicals for reducing viscosity, are not essential measures.

There are, however, frequent cases in Roumania when drill-pipe has twisted off, or otherwise parted in the hole, and the top of the fish cannot be found, not only with an over-shot, but even with an hydraulic hook. This condition of the hole is probably caused either by washing away of the walls or, what is more likely, the dissolving of the shale walls. It is noteworthy that it is in shale formations that such a large hole is usually found. In any case, the result of a twist-off at such a point nearly always means a side-tracking job, thus considerably increasing the drilling time and the drilling cost of the well. It is probable that such enlarged holes cause many breakages, owing to the violent whip which can take place in the drill-pipe at that point. No doubt such a condition of the hole can only be prevented by using a mud having the right characteristics.

I make no apology for having taken up so much of your time with the problems of drilling mud, being of such primary importance in making the drilling of deep wells an economic operation.

*Casing Programme.*—Passing to other questions, the selection of the casing programme will have an important bearing on the cost of the well, and, to some extent, on the drilling time.

At the test wells in a new area one should be willing to be more lavish in casing expenditure, as one will then have more possibilities of dealing with unforeseen eventualities. After the required information is obtained from the first wells, the casing programme can be cut to a minimum within the bounds of safety.

Many wells in the Boldesti–Harsa field have been drilled with a comparatively inexpensive programme, which allows for shutting off the most troublesome of the shales as soon as they are passed, and yet allows of the satisfactory completion of the well near the base of the Meotic. The programme in question provides for a surface string of about 200 metres of 14 in., then 1600–1800 m. of 8½ in., set below the heaving shale, and the completion of the well with a 5½-in. liner. The length of this liner is often 800–900 m., and it is, of course, cemented. I have not heard of a similar programme being used in any of the deep fields of the United States.

*Straight Drilling.*—We now arrive at the question of straight drilling. No one will deny the advantages of a straight hole, both during the drilling

life and the production life of a well. However, if sharp changes in angle or kinks are avoided, it would appear as though considerable deviations are possible without bringing about mechanical dangers.

The practice now usually adopted of employing long, heavy drill collars above the bit keeps holes reasonably vertical, and at the same time, by keeping the string of drill-pipe in tension, reduces drill-pipe troubles.

*Steam Supply.*—Passing to the steam-supply question—a particularly important one in deep-well drilling—the necessity of an adequate supply of high-pressure steam is obvious to those who have been responsible for drilling deep wells. Considerable time can be saved in pulling out, and, where much coring is necessary, this will amount to an important saving on the whole well. But the adequate steam supply is more important to enable a big volume of mud to be circulated, although quantity of steam is not sufficient unless it is at high pressure; otherwise small liners and plungers have to be used, resulting in low delivery. It is surprising how the steam supply is affected by the quality of the fireman. A good fireman watches the sequence of operations at the well and is prepared for big demands of steam, and uses the periods of low demand for feeding the boilers.

As overall steam charges are high, it is not surprising to see that a few of the companies in Roumania treat boiler-feed water. This is also done, but apparently not to a very great extent, in the United States. On the other hand, in U.S.A. superheaters of a portable type are being used, and their use seems to be on the increase.

Although this whole question of steam supply is really an auxiliary to deep-well drilling, yet it is a very important auxiliary, and warrants attention, and it is hoped that this question will not be overlooked in the ensuing discussion.

As the deep wells result in the putting of more power under the driller's control, it is now important that he should know what is happening, so that at most deep wells the group of instruments set up in front of the driller includes not only the weight indicator, but also gauges showing the mud pressure, steam pressure on the line and steam pressure after the throttle valve, also, in some cases, a revolution counter-driven from the rotary table. These instruments are not a luxury, but a necessity in the plan to eliminate hazards.

*Plant and Equipment.*—As regards derricks, one is not likely to use derricks which will not stand the heavy loads imposed in handling heavy strings of drill-pipe and casing, but sometimes the foundations are neglected, and a certain amount of uneven settling results. This will probably result in a slowing-up of operations, due to the impossibility of centring the crown block, so that delays are caused in setting slips and closing blow-out preventers. Attention to the foundations, the making of a cement apron under the derrick floor and proper drainage arrangements will save a lot of future trouble. The need for care is especially emphasized when foundations are made in the winter.

Manufacturers have come well to the aid of the drillers. Firstly, in supply of grades of drill-pipe which will complete deep wells in quick time with a minimum of accidents considering the difficulties encountered, and also in supplying full-hole tool-joints, which have enabled us to circulate bigger volumes of mud at lower pump pressures. Incidentally, the trouble

of drill-pipe breaking in the tool-joint seems to have been partly overcome by welding the tool-joint to the drill-pipe. Also, as a result of the difficulties met in deep drilling, it is now much more usual practice to make up tool-joints on a new string of drill-pipe on a machine, where the torque applied can be measured.

Secondly, the construction of draw-works in their present form, *i.e.* with a sturdy A-frame; a Hydromatic brake to increase safety and reduce brake costs; enclosing the parts to protect chains and brakes; arrangements for lubrication of the chains—all these have done much to increase all-round safety, speed, and at the same time reduce costs on the upkeep of the outfit.

In opening this discussion on deep-well drilling, I appreciate that several important considerations have not been raised, among them being the special technique involved in the actual drilling, this technique covering, as it does, such questions as types of bits, weight on bit, table revolutions, coring, the reduction of actual drilling time (especially its relation to speeding-up pulling out and running in) and many other problems which, it is hoped, will be referred to in the ensuing discussion.

Mr. J. L. Chaillet said : Mr. Elias has not given us a paper, but has been good enough to give us points to form a useful basis for discussion. I would like to congratulate Mr. Elias on the short but very clear way in which he has touched upon the most important points of deep drilling.

There is one point to be raised about casing programmes. I quite agree that where one starts a more or less unknown structure, it is a good policy to adopt a safe casing programme, instead of adopting for the first wells a programme which is influenced too much by the economical view.

I have the impression that Mr. Elias, when he speaks of the Harsa region, thinks of the present casing programme as opposed to the original programme which was used in the first years in that field. I am not convinced that the programme adopted in Harsa to-day by some companies is the best, and perhaps one has been misled by reasons of so-called economy. It is quite clear that a simplified casing programme can often reduce the drilling time, in addition to effecting a saving in casing itself. When a decision is taken on a casing programme, it is important to regard not only the drilling aspect, but also the production aspect.

After all, the drilling of a well takes three or four months or, with bad luck, five to six months; but we must remember that the well might be expected to produce at least five years. So that the casing programme adopted should have in view that the well should give no trouble due to casing during a prolonged production life.

As in everything else, we must look for a happy medium, but if there is to be a definite policy, it should be towards making the well safe for its whole life, rather than the adoption of a false economy when drilling.

I have two instances in mind where, after a year and even less, the cemented liner has collapsed. I wonder whether Mr. Elias will agree with me that such cases of collapsed liner could have been prevented by spending some more money on drilling the well and setting the water string lower down ?

Then there is another point of great interest—that of mud. From being what field-men used to call " mud troubles," we have reached a real mud

problem, and since mud reached the stage of being a technical problem, progress has been remarkable. But we should not pat ourselves on the back too much, as we still know too little about this subject. Undoubtedly with the aid of a good laboratory one can carry out a lot of experimental work on the muds, and such work will be of considerable assistance to the drillers. But I have the feeling that there is too large a distance between the laboratory and the executive at the well.

*Personnel.*—The last point I wish to raise is that of personnel. I certainly appreciate the quality of the drillers we have in Roumania. Some of them are exceptionally good, but I rather think that what we feel is lacking is that our drillers generally have too little schooling behind them to fit in with the solution of the problems which come to them under present methods.

There is here, in my opinion, far too wide a gap between the driller and the engineer. These people do not understand one another well enough; one has to listen and the other to give orders. But I cannot help feeling that there should be more collaboration between these two groups of men, because the driller, by virtue of his work, can often make very useful suggestions based on his observations. There is, I think, a way out of this difficulty, but a result cannot be reached in less than two or three years. The solution which I have in mind is that before an engineer is considered fully qualified, his education should have included such work as will have taught him not to be too proud to dirty his hands and to soil his finger-nails.

The technique of drilling is not standing still; it is progressing continuously. We want more precision and better drilling generally. So we come to the other side of the question, and must train a type of driller who will consider his career an honourable one and feel proud of it.

The schooling of drillers goes far behind the point which it did some years ago, and many drillers take an intelligent interest in the various instruments, etc., with which they are provided to improve the practice of drilling. But I feel that, as drilling technique is advancing so rapidly, a man, before he becomes a driller, should have an even better education than he does to-day. After all, we entrust to our drillers investments representing several millions of lei, and, what is more important, the lives of several men, so that we should be prepared to see that drillers have the best preparation possible to fit them for their position.

Mr. E. Boaden, B.Sc., said: Mr. Elias has directed our attention to the many problems to be faced in order to complete successfully the drilling of a deep well, and has indicated the most successful line of attack to be followed in solving these problems. He emphasizes the importance of minimizing accident risk, and, since nothing increases the cost of drilling like accidents and their attendant delays and swollen wage-bills, I propose to say a few words about one of the main causes of delays and possible accidents—that is, the perforation of high-pressure sands without sufficient preparation.

It is a well-known fact that most blow-outs occur when the situation at the well is such that the crew are in the worst possible position to deal with it, *i.e.* the drill-pipe is out of the hole, is just on the way out, or is being run in. The explanation sometimes given has been that the bit has become balled up, and on pulling out has produced a suction action in the hole, which

has induced gas to come out of the sand and follow the bit to the surface. The driller usually has orders to wash the hole before coming out with the bit when drilling through the sand, and I think it likely that most blow-outs under the above conditions are due, not to a balled-up bit, but to the withdrawal of the bit before a complete circulation of the mud has been made. If the mud is at all gas-cut, and complete circulation is made, the driller has ample warning from his mud-weight tests, and is able to add weighting material, and so control the situation. It may not be generally realized what a large volume at atmospheric pressure the gas from a high pressure sand can occupy when it is washed by the drilling mud to the surface.

For example, the drilling through with a 230 mm. bit of 10 metres of sand of 30 per cent. porosity, containing gas at 180 atms., releases into the drilling mud a volume of 0·415 cu. m. gas or liquefied gas. This swells to a volume of 22·5 cu. m. by the time it reaches atmospheric pressure at the well-mouth, and this is sufficient to occupy the annular space between 4½ in. D.P. and a 230-mm. hole over a distance of 720 m. Such a plug of gas would not, of course, all reach the surface at the same time, but would arrive cutting the mud to an extent more or less proportional to the rate at which the bit is drilling through the sand. Therefore, for this reason, it is good to retard the rate of drilling through the high-pressure sands. The slower drilling also allows the slush time to mud off the walls of the hole. At the same time, the bit should not be pulled until it is certain that a complete circulation of the drilling fluid has been obtained. A few years ago it was considered dangerous to keep the drill-pipe hanging about in the hole too long, in case of sticking, but since more attention has been paid to mud conditioning, the elimination of cuttings by means of shaking screens, etc., the danger of sticking is very much reduced.

With regard to drilling through low-pressure sands at great depths, it seems to be current practice in some foreign fields to use oil as drilling fluid for this purpose. In some cases I believe special oils have been made up by refineries. The adoption of this practice would mean the changing of the usual casing programme now used in Roumania, since combination strings with perforated pipe through the sand could no longer be used.

Certain wells in Roumanian fields have now been finished in this way, and I understand that drilling time through hard sands has been exceptionally fast.

Mr. Braileanu said : In his interesting paper Mr. Elias has paid much attention to the caving of holes, and stated that it can be avoided by giving especial attention to the mud. This is a very important factor for keeping a hole in good condition, but in the U.S.A. the technical men have not only considered the drilling mud, but have used other means for reconditioning a caving hole. Among these is the use of special tool-joints for keeping a continuous circulation while drilling or reaming a caving hole.

During the reaming of a caving hole, the stopping of the circulation for ten to fifteen minutes while adding on a piece, results in a loss of circulation and sometimes the loss of hundreds of metres of hole. By keeping a continuous circulation it has been possible to obviate this and good results have been obtained.

MR. M. METSH said : Mr. Elias raised the point of running in long 5½-in. liners. I would like to add that those cementing jobs are done through drill-pipe which is withdrawn immediately after cementing. I would like Mr. Elias's opinion on the welding of tool-joints on drill-pipe. I do not know if this procedure spoils the grain structure and produces stresses on the surface of the drill-pipe. I have heard of making tool-joints in one piece with drill-pipe, which would, of course, do away with the whole problem.

There is a practice in the States which involves the use of separate engines for driving the rotary table, and sometimes the steam pumps. Perhaps Mr. Elias has figures regarding these economies. I believe it is economical to use diesel engines and motors, at least for leases of exploration wells.

MR. CALLEYA, said : I agree with Mr. Chaillet about a large liner. I had an opportunity of making a comparison between the programmes of different companies. I found that larger-sized liners get larger production. Therefore I doubt whether economizing in size is advisable.

Most companies are drilling with steam. Recently, large-sized boilers and Wilson–Snyder pumps have been used. A 4-in. line was used for bringing steam from boiler station to well. I do not know whether this always gives good results, but we made some calculations which seem to show that the quantity of steam which gets through such a 4-in. line is sufficient to drive Wilson–Snyder pumps. Are other companies using 4-in. lines with good results ?

MR. C. R. YOUNG asked why chemicals were not used to any great extent in Roumania for breaking the viscosity of drilling muds ?

MR. M. CONSTANTINESCU said : The practice of employing drill collars is based on the plumb-bob principle.

The drilling string is kept in tension and solely for the transmission of the torque, while the necessary weight on the bit is given by the concentrated weight of the drill collars right above the bit. In order to obtain the necessary weight, it is sometimes advantageous to use oversize drill collars and long drill collars.

The limit of drill-collar length which can be carried above the bit is given by critical length above which the drill collar will bend under own weight. It is possible to calculate it by using the Euler formula for columnar stress modified by Vianello for free columns charged uniformly on the whole length

$$P = \frac{18{\cdot}75}{n} \cdot \frac{EI}{l^2}$$

Where $P$ = total load, $E$ = elasticity modulus, $n$ = safety factor, and $EJ$ = moment of inertia.

It gives for 4½-in. A.P.I. drill collar . . . 44·7 m.
5 19/32-in. „ „ . . . 51·0 m.
6⅝-in. „ „ . . . 57·0 m.

If weight carried on the bit exceeds the weight of such lengths, the drill collars will flex and tend to drill a crooked hole.

Drill-pipe failure has been very much reduced, and some of the types of failure have been almost eliminated, but there is still one type which up to now has baffled all attempts to eliminate it: failure in the upset.

It can happen in any normal thread, and our most frequent failures have been when the pin has come out of the tool-joint and left about 20–30 mm. of pin still in the box. They are typical fatigue failures, but there is not general agreement as to the reasons causing them. A small body of opinion attributes all the blame to the mounting of tool-joints on the rig.

When the tool-joint is mounted on the rig, insufficient care is taken in cleaning the threads, and if they are mounted at the well mouth, any flexing of the joint in the derrick will damage the thread, and that will cause galling. Also the lubricant used is very often of poor quality. Only zinc-base lubricants should be used. Zinc gets embedded in the threads, and cannot be squeezed out by any pressure. This is not the case with other lubricants. Even using the best of lubricants, when the threads are made up by the cathead in jerks, another difficulty occurs. When stationary, the threads tend to seize, and a sudden jerk will cause some galling, and following jerks will cause an increase of it.

The remedy for this is the simple one of putting on the tool-joints in the machine shop with a continuous motion and make them tighter than they will be made in the normal course of drilling—18,000–25,000-ft.-lb. (3300 kg. m.).

But failures still occur, and we think some other explanation is to be given which is connected with the normal work of the drill-pipe in the well.

While bending affects all threads alike, the torsion affects the threads differently. The load is transmitted from drill-pipe to the tool-joint and vice versa by the thread friction. This will bring a relative circumferential motion of the threads, which decreases with the depth of the pin in the box, and that will bring fatigue.

Also, the tool-joint is short and rigid, and will not bend; the drill-pipe, being flexible, will bend, and therefore the drill-pipe section nearest the first engaged thread will work under high bending stress. This will have one of two effects. Either it will expand the tool-joint collar and damage the threads, which will hold less and less until the length of the engaged pin is sufficiently reduced to cause failure by overload and fatigue. Or, if the tool-joint will not expand, the drill-pipe will be fatigued at the root of the first engaged thread, and give way in that place.

The matter is made worse by the sharp angle notch effect of the thread, which causes a stress concentration at the root of the thread up to $2\frac{1}{2}$ times the normal stress; also by dissolved salt and oxygen in the drilling mud. In an attempt to overcome this, the tool-joint has been welded on the drill-pipe.

Although theoretically wrong, because the grain structure of the drill-pipe is altered, it has given good results. But finally the drill-pipe may give way at the root of the weld.

Some other improvements have been tried in the design of the tool-joint, but the results are not certain, and probably a radical change in the drill-pipe tool-joint connection is required before all trouble can be eliminated.

Mr. G. Elias, in reply to the discussion, said: Mr. Chaillet raised the question of casing programmes; I think that this problem brings us a good deal of worry. It

cannot be disputed that any casing programme which will result in the failure of a well before natural exhaustion will be a false step towards economy.

Referring to the question of long liners, it is very difficult to say why there should be failure due to this programme, nor have I experienced any failure directly attributable to such a programme. However, it might be considered that a well is better consolidated when the water string is carried down to the top of the producing formations and cemented there, than is the case when the water string proper is cemented higher up, and a long liner run and cemented from above the producing formation up to the shoe of the water string. I do not see the justification of such a consideration, as the fact that the lower part of the hole is cased by the liner implies that the diameter of the pipe is less, and therefore stronger against collapse, if reasonable thickness of pipe is used.

Mr. Chaillet also mentioned tests on mud samples, emphasizing the disadvantages encountered when the laboratory is far from the rig. I agree that the mud laboratory should be in the field and, in my opinion, it should be under the charge of the drilling engineer, who can then study the problems both at the well and in the laboratory, and thereby co-ordinate the data. If he is responsible for the laboratory tests and conclusions, he is much more likely to see that the results of the tests and experiments are incorporated into practical instructions which are carried out at the rigs under his charge. A great advantage in having the laboratory near the rigs is that the mud samples can be brought fresh to it.

Mr. Chaillet brought up the important point of having properly trained and reliable drillers, as they are the men who are in charge of the big investments which lie in drilling wells and equipment. In my opinion, drillers who have qualified as such within the last four or five years show much greater intelligence than those employed ten to fifteen years ago. I think that the drillers who are qualifying now are of a better type, and are proving themselves to be very capable men. On the other hand, progress in drilling and production technique is so rapid that possibly the schooling which drillers and foremen get is not sufficient for present-day requirements. Unless the teaching is quite up to date they will be three or four years behind present requirements. As regards the older drillers and foremen, it is too much to expect that they should go back to school now to try to acquire the technical knowledge demanded by present-day methods. I think that drillers and foremen are making determined efforts to keep up with progress and the drillers' schools are probably doing what they can, but if more could be done we would get better results.

Mr. Boaden especially emphasized the importance of drilling slowly through high-pressure sands. I quite agree, and believe that many drilling engineers to-day insist on this. I had never thought of the interesting example he gave of the amount of gas which would be released from the comparatively small hole which is drilled.

Mr. Metsch mentioned the possible bad effects of welding tool-joints to drill-pipe, due to the heat treatment originally applied to the latter. When one hears to-day so much about heat treatment, it might be thought that the welding would undo some of the good done, but in practice such bad effects are not apparent. The method is widely used in America, and is now being tried out in Roumania, so far with good results. One has now to find a solution to the difficulty of mud cutting out the tool-joint threads. This is a problem which has arisen only since big volumes of mud are circulated. The welding of the tool-joint to the drill-pipe has eliminated the cutting of the thread at that point, and seems to have overcome the constant breaks of drill-pipe pins, the most frequent cause of twist-offs in recent years. These two advantages are so marked that the possible disadvantage of damage to the heat treatment has not been noted.

Mr. Metsch also mentioned the use of diesel power units for drilling wildcats. Here we have not had much difficulty with the fuel supply for wildcats, as the latter have, so far, been nearly all comparatively near to existing exploitation, and one can either make a gas line or truck fuel oil. From the many perimeters granted by the State, we can see that the near future will see many wildcats far from existing production, and I agree with Mr. Metsch that diesels may be the best solution to the problem of drilling distant wildcats.

Mr. Constantinescu, in raising the question of drilling straight holes, mentioned a formula with which I am not familiar, but which is certainly interesting. The accepted method for drilling straight holes appears to be to use plenty of weight immediately above the bit; it keeps the string in tension, which is apparently what is wanted, is simple and gives a good result. However, other factors undoubtedly come into the problem, and I am sorry that no one has raised the question of the effects of pumps speeds and table revs. on the deviation of a hole. Another question raised by the same gentleman—that of tool-joint lubrication—is very important under the present system of making-up and breaking-out by mechanical means. Quite rightly he also emphasizes the need of proper means for putting tool-joints on to drill-pipe; that is to

say, they should be made up on a machine which applies a controlled torque. This measure, together with that of welding tool-joints to drill-pipe, has done much to arrest the number of accidents due to breakage of drill-pipe pins.

Mr. Young asked about the employment of viscosity breakers for mud in this country. I have had little experience of the use of these, but what I have had indicates that the natural muds do not usually require such chemical treatment.

As a new measure of economy Mr. Calleya suggested the suppression of reaming. I think that this is a direction in which we can really economize. A number of accidents can be attributed directly to reaming, and reaming occupies quite a lot of time. The accidents have usually been breakages of drill-pipe pins during reaming, and when discussing this question with an engineer of a large pipe factory in America, I was informed that similar breakages during drilling have become more prevalent since contractors have been obliged to drill straight holes, resulting in less weight being put on the bit, as in reaming. It is supposed that during drilling and reaming vibrations are set up in the drill-pipe, but these vibrations are damped when more weight is put on the bit, or, conversely, when the tension in the drill-pipe is increased. For these two reasons I support Mr. Calleya's suggestion, but we must remember that running the bit to bottom, although usually called reaming, is simply conditioning the mud. In such operations the speed of rotation need only be low.

Mr. Calleya also mentioned the studies he had made on the effect of casing programme on ultimate production. He has reached the conclusion that a well with bigger casing through the sand will give a larger ultimate production, other things being equal.

I cannot agree with Mr. Calleya on this point. I saw a large amount of data on this question from one of the important fields here, and came to the conclusion that one could not find any relationship between the size of the hole and the production obtained.

With regard to the last question—that of size of steam line between boiler-house and rig—my experience is that 4-in. pipe is usually rather small, although the working pressure employed will influence one's choice.

# A NEW TYPE OF THREADED CONNECTION FOR OIL WELL CASING.*

By W. M. Frame.

A new type of threaded connection for use on oil-well casing is being successfully used in the Mid-continent, Rocky Mountain and California fields of the United States, as well as in certain foreign countries, including Ecuador and Japan. Casing equipped with this new thread is known as "Extreme Line Casing," and considerably more than half a million feet of this casing had been used prior to January 1st, 1937, in sizes ranging from 4½ inches O.D. to 10 inches O.D.

The casing joint comprises an upset, threaded pin end and a mating upset, threaded box end as shown in Fig. 1. There is no coupling. A modified Acme type of thread form is used in conjunction with a conical seal. Thus, the two main functions of the joint—namely, mechanical strength and resistance to leakage, are taken care of by separate means. A shoulder is provided on the pin member which engages the end of the box member when made up so that there are no abrupt changes in contour. The outer surface is turned, and the inner surface is bored to ensure joint dimensions of greater accuracy than is obtained on the usual type of threaded and coupled joint.

The major advantages of this new type of casing joint as claimed by the manufacturers in comparison with the usual V-threaded type are as follows :—

Higher joint strength.
Smaller outside diameter at the joint.
Higher resistance to leakage.
Greater resistance to accidental damage.
Stream-lined contour inside and out.
Greater speed in running.

The high joint strength permits long strings to be run with large factors of safety in tension. The joints are so proportioned that the joint strengths in tension are very nearly the same for all weights of casing of the same grade manufactured in any one size. This means that relatively thin-walled casing can be safely used in the upper part of a string to support the thicker-wall casing that must be used in the lower part of the string to resist collapse.

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* Paper presented at a Meeting of the Institution of Petroleum Technologists in London on May 4th, 1937.

FIG. 1.
A NEW TYPE OF CASING JOINT.

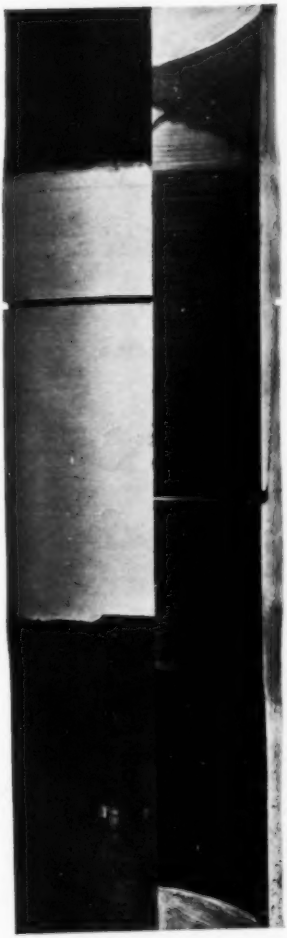
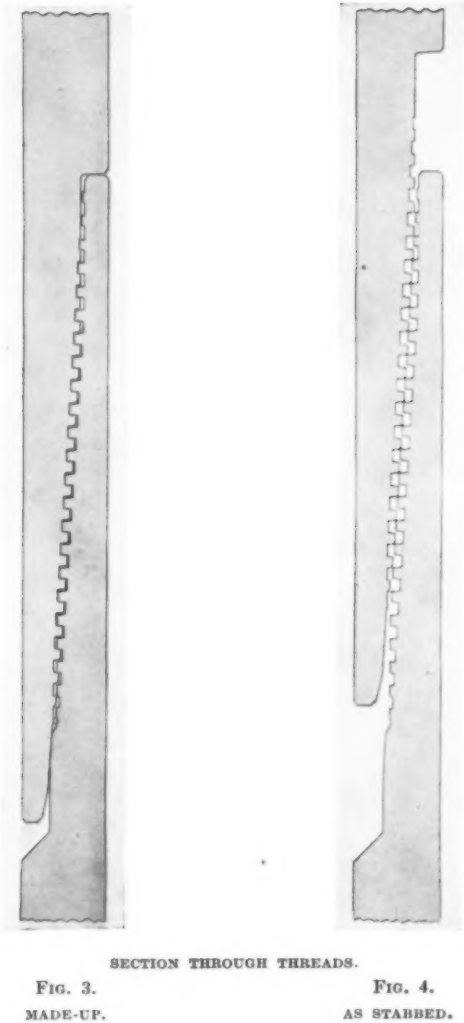


FIG. 2.
HALF SECTION OF JOINT, HAND-TIGHT.

[*To face p.* 422.



SECTION THROUGH THREADS.

FIG. 3. MADE-UP.

FIG. 4. AS STABBED.

The joint Efficiencies of Extreme Line Casing in some of the sizes now manufactured compared with A.P.I. Casing are as follows :—

| Size O.D., ins. | Wt. per ft. Extreme line, lbs. | Joint efficiencies. Regular threads A.P.I. | | Extreme line. Grades C or D, %. |
|---|---|---|---|---|
| | | Grade "C." %. | Grade "D." %. | |
| 4½ | 16 | 65 | 63 | 86 |
| 5 | 20 | 63 | 61 | 87 |
| 5½ | 22·50 | 62 | 60 | 87 |
| 6⅝ | 28 | 60 | 58 | 84 |
| 7 | 30 | 59 | 57 | 81 |
| 7⅝ | 33·70 | 58 | 56 | 81 |
| 8⅝ | 43 | 55 | 54 | 75 |
| 9 | 45 | 54 | 53 | 76 |

$$\text{Joint efficiency} = \frac{\text{Strength of joint}}{\text{Ultimate strength of pipe}}.$$

The outside diameter of the joint is considerably smaller than that of the coupling usually employed on casing. This is permitted by the use of the upset end, the Acme type of thread and the close-machined tolerances on the outer and inner surfaces. Smaller outside joint diameters allow greater clearances between strings, and in some cases the manufacturers claim that smaller outer strings may be used with adequate clearances.

The outside diameter of the joint is the same as for all the various weights of casing manufactured in any one size. The inside diameter of the joint is slightly smaller than the nominal inside diameter of the pipe. However, the joints will pass the A.P.I. drift specified for the pipe except the lightest weight in each size, in which case the drift for the next heavier weight must be used.

High resistance to leakage is obtained by means of the conical sealing surfaces. The engagement of these surfaces can be seen in Figs. 2 and 3, near the end of the pin member. The sealing surfaces are very accurately machined to a smooth finish. They are so proportioned and located with respect to the rest of the joint that they are not susceptible to accidental damage. According to tests made by the manufacturers, the joints do not leak when subjected to external pressure sufficiently great to collapse the pipe, nor internal pressures that stress the pipe beyond the yield point.

The shoulder on the pin member and the non-engaging nose extending beyond the sealing surface help to protect the joint from accidental damage. Also, the modified Acme type threads are of coarse pitch, with wide crests, and are not as easily damaged by accidental blows as the sharp V-thread. There is a small clearance between mating flanks and mating crests and roots, as can be seen in Figs. 2 and 3. This clearance provides room for small amounts of foreign material or for small burrs to flow into during make-up. Without this clearance small burrs or deformations caused by accidental blows might seize and cause galling.

The upsets are proportioned to provide stream-lined contours on both outer and inner surfaces. This may be important where there are restrictions or junk in the hole. The square shoulder represented by the end of

the usual type of coupling sometimes hangs up on projections in the hole, and causes trouble. Also, it is claimed that with certain hole conditions circulation can be more easily established than with the usual collared casing.

This type of joint makes up very rapidly, and enables the operator to run a string in less time than is usually required. This is because of the coarse pitch and shallow depth of the thread and the steep taper. As compared with the usual V-thread, the pin stabs farther into the box, fewer turns are required from stabbed position to rope-tight position, and less than one turn of power tonging is necessary. Make-up is limited by the shoulder on the pin member, so that the operator cannot overtong the joint. Fig. 4 shows a partial section of the joint in the as-stabbed position. Fig. 2 shows the joint hand-tight, and Fig. 3 shows the joint made up.

An example of the weight and clearance economies effected by the use of this joint in a deep well is shown in Table I. In the first programme the three strings of casing are according to A.P.I. Standard. In the second programme the outer string is A.P.I. and the two inner strings are Extreme Line. The casing programmes used in this example are imaginary ones, and it is recognized that a saving of as much as 20 per cent. by weight cannot usually be obtained. However, the example illustrates the point that in many instances the advantages of this new type of casing can be realized at no greater over-all cost, and often at a material saving.

Pup joints of Extreme Line Casing are furnished, and there are also available accessories for use with this type of casing joint, such as casing shoes, cement shoes, float collars and whirling cement collars.

It may be interesting to mention a few instances of service secured with this type of casing.

A string of 10,815 ft. of 6⅝ inch × 26 lbs. Grade "D" Range three Extreme Line Casing was run in a well at Kettleman Hills, California, in December 1935, and at that time was the longest string ever run in any well. It was remarkable that this 6⅝ inch was run inside a string of 8⅝ inch × 36 lbs. Casing set at 9081 feet, below which a 7⅞ inch hole had been drilled to 10,828 feet, so that the clearance between the open hole and the outside diameter of the extreme line joint was at a minimum. The total time consumed in running this 10,815 feet was 14 hours 40 minutes. A great deal of time was lost in running the first 800 feet, but after the crew became experienced, 284 lengths were run in 12 hours 44 minutes, or at the rate of approximately 10,000 feet in 12 hours.

In another Kettleman Hills well a string of 7 inch O.D. × 30 lbs. Grade "D" Extreme Line was run to 8500 feet in a hole where three bad fishing jobs had previously occurred, resulting in a considerable amount of material being sidetracked. At about 8035 feet the cement equalizers welded to the bottom of the string stuck, and the whole string had to be pulled. After about 40 minutes very hard pulling, the string came loose. All joints were examined as they were unscrewed, but were found to be in perfect condition, and the whole string was set about three weeks later.

A company in Texas used a considerable amount of 6⅝ inch × 26 lbs. Grade "C" Extreme Line Casing. At the commencement the crews found no difficulty in running this pipe at approximately 1000 feet per hour, 6 hours being considered standard time for setting 6000-foot strings,

as compared with 10 to 12 hours required for setting similar strings of A.P.I. Casing. With greater experience the crews have been able to set 6000 feet of this size Extreme Line in under four hours.

In California 8¼ inch × 36 lbs. Extreme Line has been subjected to severe service as washover pipe. During a period of one month this string made forty-five trips into the hole, recovering 5 9/16 inch drill pipe which had been dropped and badly kinked. The 5 9/16 inch was recovered from 2500 to 6048 feet. The service was extremely severe, as each joint of the casing had to be unscrewed with the kinked 5 9/16 inch inside, which caused it to be unscrewed out of alignment.

These few examples demonstrate some of the advantages which are offered by the use of Extreme Line Casing, one of the principal of which, as will be seen, is the saving in time in running and pulling when compared with regular collared casing.

TABLE I.

| Type of joint. | Pipe O.D., in. | Weight per ft., lbs. | Length, ft. | Depth set, ft. | Coupling or joint O.D., in. | Pipe I.D., in. | Clearance on diam., in. | Joint strength in 1000 lbs. | Factor of safety. | | Weight string, of lbs. | Weight of programme, lbs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Tension. | Collapse. | | |
| A.P.I. long | 13¾ | 61·7 | 4000 | 4000 | 14·375 | 12·515 | 1·89 | 825 | 3·35 | 1·22 | 247,000 | |
| A.P.I. long | 9⅝ | 47·6 | 6000 | 6000 | 10·625 | 8·681 | 1·29 | 855 | 2·98 | 1·67 | 286,000 | |
| A.P.I. long | 6⅝ | 28·1 | 8000 | 8000 | 7·390 | 5·791 | | 615 | 2·73 | 1·78 | 225,000 | 758,000 |
| A.P.I. short | 11¾ | 47 | 4000 | 4000 | 12·866 | 11·000 | 1·620 | 660 | 3·5 | 1·20 | 188,000 | |
| Ex. line | 9 | 34 | 4000 | 4000 | 9·380 | 8·290 | | 990 | 4·6 | 1·78 | 136,000 | |
| Ex. line | 9 | 40 | 2000<br>6000 | 6000 | 9·380 | 8·150 | 1·22 | 1035 | — | 1·58 | 80,000 | |
| Ex. line | 6⅝ | 24 | 6500 | 6500 | 6·930 | 5·921 | | 690 | 3·5 | 1·73 | 156,000 | |
| Ex. line | 6⅝ | 28 | 1500<br>8000 | 8000 | 6·930 | 5·791 | | 715 | — | 1·78 | 42,000 | 602,000 |

*Note.*—All material is assumed to be A.P.I. Grade D.

Saving in weight = 156,000 lbs.
or 20%

## OBITUARY NOTICE.

### THOMAS RICHARD HENRY GARRETT, O.B.E., M.A.

On the 16th of April, 1937, there died one whose name is known to all members of this Institution, whose loss is deplored by all those members who had the privilege of knowing him as a friend or of working with him as a colleague on the Council on which he served so long and so well.

T. R. H. Garrett took his degree at Cambridge in 1902, being a scholar of Jesus College. In those days the writer first appreciated his striking personality and the enthusiasm and diligence which were so characteristic of him throughout his career.

After some post-graduate work with Sir John Murray on the Survey of the Scottish lochs, he joined the Shell Trading and Transport Co. in 1904, three years before its amalgamation with the Royal Dutch, and went out to Borneo as chief geologist, with Balik Papan as his centre.

It is difficult nowadays to realize under what difficulties a geologist in those days in such a country worked. Often for a month or two at a time Garrett worked without a white colleague in the jungle. His robust health, his unflagging energy, his knowledge of the language and customs of the natives and his marked power of utilizing to the best whatever resources he had available, contributed to the success with which he carried out his difficult task. His keen interests in anthropology and in the life of the jungle enabled him to bear easily, if not indeed to enjoy, his long periods of absence from his fellow-men. After some years of service with the Shell and later with the Bataafsche, his independent spirit led him into other directions, finding him original work in the East Indies, Malay States, Burma and Siam.

He at once enlisted at the outbreak of war. His high sense of duty and his dogged determination singled him out for rapid promotion, and after experience in the R.N. Armoured Cars and R.N.A.S., he was transferred to the R.A.F. as major, and was in Armament Headquarters in London when the war came to an end.

After the war he returned to the East, but eventually settled in London as a consultant, which resulted in his visiting Rumania and Trinidad. He thus acquired a very extensive practical knowledge of many of the oil-producing centres of the world.

He was an original member of this Institution, was elected to our Council in 1929, and took up this work with his usual enthusiasm and diligence. He holds the record for attendance at meetings on the committees which he served so well. He was a man with many interests, time never "hung heavy" on his hands. To his anthropology, hunting and photography which filled his spare time abroad, he added scientific beekeeping in his later days at home. During the long period of his illness, which his fighting spirit undoubtedly prolonged, he found solace in the stamps which his travels had given him such excellent opportunities to collect. So died a man with a physical and mental equipment which all who knew him must have admired, and with a character which those who had the privilege of his friendship will never forget. J. K.

# THE VISCOMETER WITH SUSPENDED LEVEL. (THE ELIMINATION OF THE INFLUENCE OF SURFACE TENSION BY THE SUSPENDED SPHERIC LEVEL.)

By Prof. Dr. L. Ubbelohde (Hon. Member).

In May 1933 I presented a paper on a new viscometer and other instruments using the principle of the suspended level. Since this time we have further developed the new viscometer and produced a form of the viscometer with a *spheric level*, which eliminates every correction on account of surface tension of the liquid tested.

Furthermore, we found that the factor $m$ in the Hagenbach–Couette correction for kinetic energy had the same value 1·12 for a viscometer with suspended level as for all other capillary viscometers.

In this paper we give the new development of the viscometer and the new correction table for kinetic energy, based on the factor $m = 1{\cdot}12$.

But, to simplify the argument, it will be necessary to repeat some of the calculations included in our paper of May 1933 and for basing the spheric level on similar calculations, slight modifications have been necessary.

## I. The Suspended Level in Dynamic Equilibrium.

### 1. *The Suspended Level at a Flat Surface.*

Fig. 1 shows that capillary 4 is enlarged to a circular surface *a* at the top of tube *C* of large diameter. When liquid is discharged from capillary 4, it turns through a right angle at the lower end of the capillary, and, spreading out radially, it follows the horizontal circular surface *a* to its edge. Then, bending through another right angle, it flows vertically down the wall *e* of the wide tube *c*. We shall consider this phenomenon for the case

Fig. 1.

of flow so slow that the kinetic energy can be neglected. Then the volume $V$, discharged out of capillary 4, is given by Poiseuille's formula

$$V = \frac{\pi \cdot g \cdot h \cdot r^4}{8 \cdot l \cdot \nu} \cdot t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Herein

$t$ = time of flow (seconds),
$g$ = acceleration of gravity (cm. sec.$^{-2}$),
$h$ = average head (cm.),
$r$ = radius of the capillary (cm.),
$l$ = length of the capillary (cm.),
$\nu$ = kinematic viscosity in Stokes.

The same volume $V$, after leaving the capillary, passes as a suspended layer over the plane surface, the liquid being held by forces of cohesion and adhesion. In the angle $w$, between $a$ and $e$, there is formed a ring-shaped collar, which, in consequence of surface tension, seeks to collect liquid behind it. In the vertical layer $e$ it acts against gravity, but this is not the case in the horizontal layer at $a$. Consequently flow takes place in the direction $a$-$w$-$e$, and in fact this is flow with free surface. From Newton's hypothesis there could be derived for laminar flow of a liquid in a sloping open channel the formula

$$V_1 = t \cdot d^3 \cdot b \cdot g \frac{h_1}{3 \cdot l_1 \cdot \nu} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Herein

$V_1$ = volume passing the channel (cm.$^3$),
$d$ = thickness of the liquid layer (cm.),
$b$ = its width (cm.),
$l_1$ = its length (cm.),
$h_1$ = pressure head (cm.).

(The formulæ for open channels, common in practical hydraulics, apply to turbulent flow, and are not valid here.) Therefore the value $g \cdot \frac{h_1}{l_1}$ is the attraction of gravity at every particle of the liquid in direction of flow, and it seems that this value becomes zero for the plane suspended level. But, after passing through the right angle at $w$, gravity pulls with its full value, and this pull is transmitted, in consequence of the cohesion of the liquid, to the circular surface. This force of traction is partly used to overcome the friction on the way of the liquid from the capillary to the ring-shaped collar, and therefore diminishes in the direction to the capillary axis. If this variable force is called $\kappa$ and inserted in formula (2) for $g \cdot \frac{h_1}{l_1}$, then,

$$V_1 = t \cdot d^3 \cdot b \cdot \frac{\kappa}{3 \cdot \nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since the liquid spreads from the centre to the periphery of the circular surface, the width $b$ of the path of the liquid increases constantly as the edge is approached, and (taking $r_a$ as radius of the circular surface $a$ to distin-

guish it from the radius of the capillary $r$), then $b = 2 \cdot \pi \cdot r_a$. If this relation is inserted in equation (3), we have

$$V_1 = t \cdot d^3 \cdot 2 \cdot \pi \cdot r_a \frac{\kappa}{3 \cdot \nu} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In this equation $\kappa$ increases with $r_a$. In consequence, $d^3$ (thus the thickness of the liquid layer) decreases in deviating from the centre.

Then the layer of liquid must be thicker in the centre than at the edges, and this variation in thickness must have the result that the layer of liquid, suspended under the plane annular surface, tends to take the form of a disc generated by a curved line. The formation of such a surface, however, is opposed by surface tension; for the element of this and further considerations is that the surface tension of every liquid tries to prevent the surface of the liquid assuming an inconstant shape. Both effects, therefore, acting together, determine a form of the liquid surface which does not quite correspond to the mathematical form given by equation (4). A test under conditions such as occur in viscosity determinations, where a volume of 5 cm.$^3$ was discharged out of a capillary with $r = 0{\cdot}1$ cm. under an average head of $h = 12{\cdot}5$ cm. in a time of discharge of 70 sec., gave the form of surface shown by Fig. 2. The pressure which the arched surface exerted in the direction of the capillary axis was considerable. It amounted in a similar case with water to 0·2 cm., and, being variable with the surface tension of the liquid tested, this form of the suspended level was not fit for viscosity measurements.

### 2. *The Suspended Level at a Curved Surface.*

A suspended level may also be formed if the change from the capillary to the wider tube $C$ has the shape of a hollow hemisphere as in Fig. 3.

Here equation (2) can be directly applied to the liquid discharged out

Fig. 2.

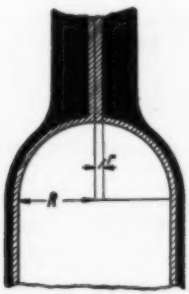



Fig. 3.

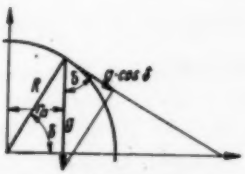



Fig. 4.

of the capillary, for the hollow hemisphere may be regarded as a real open channel. So, for instance, in every point $P$ of the inner surface of the ball, having the distance $r_a$ from the capillary axis, the liquid is drawn in the direction of flow by $g \cdot \cos \delta$ (see Fig. 4).

Now,

$$\cos\delta = \frac{r_a}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$g \,.\, \cos\delta = g \,.\, \frac{r_a}{R} \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In point $P$ the width of the liquid layer is $b = 2 \,.\, \pi \,.\, r_a$, and so equation (2) gives with equations (5) and (6)

$$V_1 = t \,.\, d^3 \,.\, \frac{2 \,.\, \pi \,.\, g}{3 \,.\, \nu} \,.\, \frac{r_a}{R} \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

as equation between the volume discharged and the thickness of the liquid layer.

Here also $d^3$ decreases with increasing $r_a$—that is, in deviating from the capillary axis.

If, therefore, the surface of the liquid was not quite plane at the flat level, it now has not quite a spherical shape, but assumes this only with increasing distance from the capillary axis. Here too, however, the deviation from the shape of a sphere is not quite independent of the value of traction, with which the surface tension draws at the point $r_a = r$, and so this arrangement seemed also not fit for viscometers.

Now, it is possible to provide the space which the liquid needs and which it otherwise obtains by deformation of the surface. For this purpose the capillary is slightly hollowed out at its lower end in a funnel-shaped form, so that a conic change exists between the capillary and the level. But it is necessary so to choose the taper that in it may be placed the amount of liquid which is otherwise placed in the deformations from the plane or from the hollow hemisphere. But to give an idea in which way the capillary must be tapered, it is necessary to consider how the generating curve of the surface may be formed. The unfavourable case may be taken where $\kappa$ is constant.*

The volume $V$ of equation (1) passes through the hanging liquid layer. Therefore, $V = V_1$, and equations (1) and (3) give

$$d^3 = \frac{r^4}{r_a} \,.\, \frac{3}{16} \,.\, \frac{h}{l} \,.\, \frac{g}{\kappa} \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Introducing $r_a = \beta \,.\, r$ and, for sake of simplicity, letting $\sqrt[3]{\frac{3}{16} \,.\, \frac{h}{l} \,.\, \frac{g}{\kappa}} = C_1$ we have

$$d = r \,.\, \sqrt[3]{\frac{l}{\beta}} \,.\, C_1 \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

* Already in equation (3) it has been shown that $\kappa$ diminishes in the direction of the capillary axis and increases with increasing $r_a$. These influences together have the effect that $d$ becomes rapidly very small; a fact which is very favourable for the planing of the hanging surface of the liquid at the plane annular surface, as may be seen from the following. So we would reach our goal much easier if $\kappa$ and $r_a$ are variables.

But the function between $\kappa$ and $r_a$ is very complicated, because the cohesion of the liquid is certainly not constant with different thicknesses of the liquid layer, for the influence of the liquid layer at the interface between liquid-solid is unknown and because on the annular surface there is no constant velocity distribution of flow.

This relation is shown in Fig. 5. The curve is the generating curve of the surface of the liquid, shown on an enlarged scale. To obtain the real film thickness, and thus to calculate the true amount of liquid to be placed in the funnel, the ordinates $d \cdot \frac{1}{r \cdot C_1}$ must be multiplied by $r \cdot C_1$. But $C_1$ contains the unknown value $\kappa$, corresponding to the tractive force in the spreading film. Even after determination of all values for a given case, its

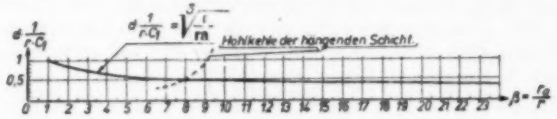



FIG. 5.

calculation would be very difficult, probably impossible. But such a calculation is not necessary. For further consideration shows that the end of the capillary should not be tapered less than enough to make room for the liquid disc, but it may be tapered out more; it is therefore hollowed out considerably, similarly to funnel $T$ in Fig. 6.

At the part $a_1$–$a_2$ of the circular surface the liquid surface may perhaps show some slight deviation from a flat surface. But the generating curve of the liquid surface runs with an increasing radius more and more asymptotic to the horizontal circular surface; consequently the liquid surface between $a_1$ and $a_2$ is almost flat, and in the case where the radius $r_{a_1}$ is large enough, the liquid surface is no longer arched below the opening of the

FIG. 6.

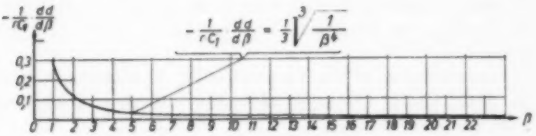



FIG. 7.

funnel $T$. Such a flat surface, however, does not result in pressure action, due to surface tension, in the direction of the capillary axis (that is, perpendicular to it), and so the average head is no longer affected to a noticeable degree.

As it is of interest to test the change in thickness $d$ between $a_1$ and $a_2$ (or, in general, between two different radii $\beta_1 \cdot r$ and $\beta_2 \cdot r$), let us take the differential quotient $\frac{dd}{d\beta}$. Then

$$\frac{dd}{d\beta} = -r \cdot C_1 \cdot \frac{1}{3} \cdot \sqrt[3]{\frac{1}{\beta^4}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Fig. 7 shows the curve given by equation (10). It is noticeable how quickly the curve falls at first, and then approaches asymptotically the value zero. This means that a change of $\beta$ causes only a very small change of $d$, even at small values of $\beta$, and that this change of $d$ with $\beta$ approaches rapidly to zero. A test with an average head of $h = 14{\cdot}0$ cm., a radius of the opening of the funnel $r_{a_1} = 0{\cdot}225$ cm. and $\beta_1 = \frac{r_{a_1}}{r} = 4{\cdot}5$, showed that the thickness of the liquid layer, measured with telescope and scale, was all over smaller than 0·01 cm. If we put this value in equations (Hohlkehle der hängenden Schicht—Concavity of the suspended layer) (9) and (10), we find that the decrease in $d$ equals or is less than 0·0074 times the increase in $\beta$, even without considering that we should have given the value $\beta = \frac{1}{2}(\beta_1 + \beta_2)$ in the equations. Then the decrease in $d$ would be even smaller.

Thus, if by suitable form and dimensions of the capillary outlet the liquid surface under a can be so flattened that its effect on the pressure head lies far below the experimental error, then the effect becomes still smaller for the following reason. The suspended liquid layer forms at the corner $w$ a collar, concave in shape and downward in position, which also affects the suspended layer $a_1a_2$. If in Fig. 5 we represent the flow of the collar at $w$ according to its direction, we get the dotted line, which cuts the generating line of the liquid disc. If the dimensions are so selected, the two effects meet below the path $a_1a_2$ and they are partly balanced, with the result that the path $a_1a_2$ of the liquid surface becomes still more nearly parallel to the solid circular surface.

### 3. *Position of the Suspended Level.*

Finally, we find, from equation (9), the proof, important for our purpose, that the thickness of the suspended layer is independent of kinematic viscosity, specific gravity and other properties and has the same value with all liquids, so long as the dimensions and the pressure head remain unchanged.*

The thickness of the suspended liquid layer being the same for all liquids, the level lies at the same elevation for all and adjusts itself automatically with physical certainty.

This conclusion, arrived at from pure hydrodynamic considerations, is practically unaffected by the fact that the fields of molecular force at the interface between liquid and solid wall cause adhering layers of special physical properties, containing differently oriented molecules with different liquids. For in this layer it is a question of dimensions of molecular size; and it is shown in an experimental investigation not yet published that with lubricating oils, which are especially fit for forming such layers, these dimensions are in the order of magnitude of $1{\cdot}10^{-6}$ cm. and are of no influence here.

### 4. *Relation to Pressure Head.*

If we again consider equation (8), we see that $d$ increases also with $h$, but only as the cube root of $h$; for we have

* Therefore it is also unnecessary to determine where the real level, which defines the difference in head $h$, is located within the suspended layer, which would be difficult to determine on account of the parabolic velocity distribution in the capillary and the change of direction at its lower end.

$$d = r \cdot \sqrt[3]{\frac{1}{\beta} \cdot \frac{3}{16} \cdot \frac{g}{l \cdot \kappa}} \cdot \sqrt[3]{h} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and, for the sake of simplicity, with $\sqrt[3]{\frac{1}{\beta} \cdot \frac{3}{16} \cdot \frac{g}{l \cdot \kappa}} = C_2$

$$d = r \cdot C_2 \cdot \sqrt[3]{h} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$d$ is also a function of $h$. This relation is shown in Fig. 8. Also $\frac{dd}{d\beta}$ increases with the cube root of $h$. If the change of $\frac{dd}{d\beta}$ with increased pressure is not desired—that is, if the surface is not to become less flat—then from equation (10) by inserting $C_1$ we have

$$\beta^4 = h \cdot \frac{r^3}{\left(-\frac{dd}{d\beta}\right)^3} \cdot \frac{1}{144} \cdot \frac{g}{l \cdot \kappa} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Equation (13) may also be written

$$r_a = r \cdot \sqrt[4]{h} \cdot \sqrt[4]{\frac{r^3}{\left(-\frac{dd}{d\beta}\right)^3}} \cdot \sqrt[4]{\frac{1}{144} \cdot \frac{g}{l \cdot \kappa}} \quad . \quad . \quad . \quad (14)$$

The radius $r_a$ of the opening of the funnel must therefore be changed in proportion to $\sqrt[4]{h}$. Otherwise the flow will not be affected, so that the instrument is also fundamentally suitable for use with an external source of pressure.

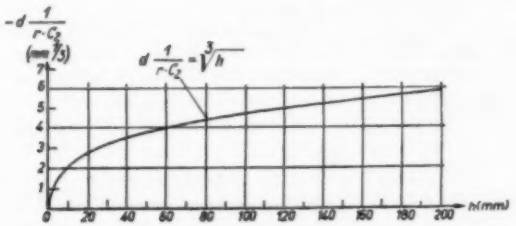



FIG. 8.

Therefore, we may state that by choosing the measurements of the funnel and the diameter of the circular surface favourably, we can flatten the hanging surface of the liquid as much as we like.

The task of shaping the hanging liquid layer in the hollow hemisphere to the form of a sphere is to be approached in the same way. Here also the volume $V$ of equation (1), after leaving the capillary, passes through the hanging layer. Then equation (1) gives with (7)

$$d^3 = \frac{3}{16} \cdot \frac{h}{l} \cdot R \cdot \frac{r^4}{r_a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which with $r_a = \beta \cdot r$ and $\sqrt[3]{\frac{3}{16} \cdot \frac{h}{l} \cdot R \cdot r^2} = C_3$ may be written:

$$d = C_3 \cdot \sqrt[3]{\frac{1}{\beta^3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Then the differential quotient

$$\frac{dd}{d\beta} = -\frac{2}{3} \cdot C_3 \cdot \sqrt[3]{\frac{1}{\beta^5}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Here also the real value of $C_3$ is not known, on account of the unknown values of cohesion and adhesion in the liquid layer. We have drawn the

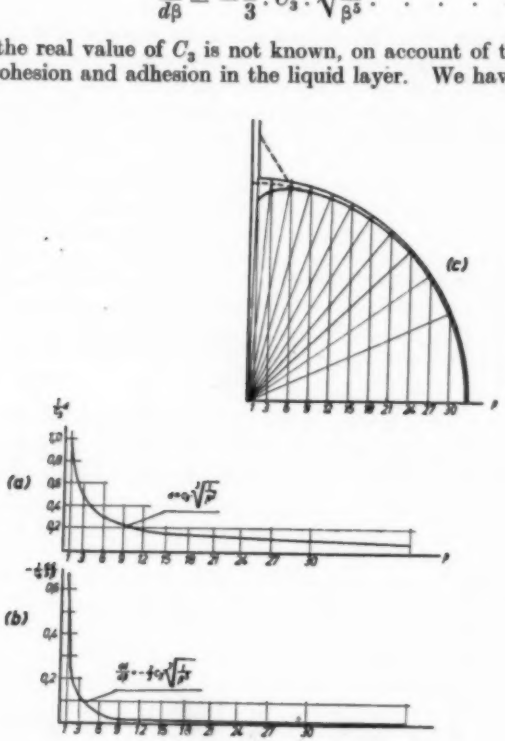



FIG. 9.

generating curve of the liquid surface for the ratio of $\frac{r}{R} = 0{\cdot}03$, which agrees with our viscometer capillary I, in a diagram having as abscissæ the parts of a quadrant corresponding to the values of $\beta$ (see Fig. 9*a*). It seems as if this curve falls much more rapidly than the corresponding curve at the flat level. But if we mark the thickness of the liquid layer on the radii corresponding to the $r_a$-values, as shown in Fig. 9*c*, it is easy to see how rapidly the liquid surface assumes the shape of a sphere. Moreover, this is emphasized in Fig. 9*b*, where again $\frac{dd}{d\beta}$ is drawn in a diagram with

parts of a quadrant corresponding to the β-values as abscissæ, as in Fig 9*a*. This curve falls very much more rapidly than the corresponding curve with the flat level. Things are therefore much more favourable here than with the flat level.

We can expect a deformation of the liquid surface only under greater pressure heads than with the flat level, on account of the fact that in the case $r_a = r$, not only the surface tension applies a tractive action to the liquid, but also gravity $g \cdot \frac{r}{R}$. Only with relatively high pressure heads do we find a deformation of the liquid surface curved contrarily to the hollow hemisphere. In general, the sphere will only be slightly flattened, the thickness of the liquid layer diminishing, if $r_a$ increases to $R$. If here also we hollow out the end of the capillary to a little funnel, its lower radius even in a little funnel is of such magnitude that a further increase in $r_a$ results only in negligible decrease of $d$.

But even if we have a form of the liquid surface which is not quite spherical but resembles that of a geoid, the real shape of the liquid surface is still quite unimportant; for in equation (15) the kinematic viscosity ν does not appear and therefore, in this case, the liquid surface is also formed at one and the same elevation for all liquids as with the flat level.

Having already shown with the flat level that other influences are insignificant for the formation of the suspended level, we need not repeat the calculations for the spheric level.

### II. The Elimination of the Traction of Surface Tension at the Upper Liquid Surface by the Opposite Traction of the Suspended Spheric Level.

With the plane suspended level, the surface tension acts perpendicularly to the vertical—that is perpendicularly to the direction of flow—and therefore has no influence on the pressure head.

But in every viscometer we have in the upper vessel a free liquid surface, where surface tension acts with its full value. This action may be determined, for, with most of the liquids to be tested, if the walls of the vessels be wetted, the meniscus is drawn up the walls. Consequently the liquid surface is lowered and the effective pressure head influenced.

For a little tube, where the rising of a liquid on account of surface tension is great in comparison with the radius, possibly in another order of magnitude, the apparent increase of a given average head is shown in the formula

$$\Delta h = \frac{2 \cdot \alpha}{r \cdot \gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

wherein

$\alpha$ = surface tension in g.-cm.$^{-1}$ or Dyn.-cm.$^{-1}$,
$\gamma$ = specific weight.

This formula is correct only as long as the upper meniscus has a constant curvature, caused by the action of the surface tension at the interface between liquid and solid wall, as shown in Fig. 10.*

* Herein $\Delta h$ is not only to be measured up to the meniscus. Moreover, the parts of the liquid drawn up at the walls must be taken as flattened, as shown with $\Delta h$ in

In a viscometer, however, the upper surface is not in a capillary. The upper part of the viscometer consists of a ball-shaped vessel, connected with the viscometer capillary and with the open air by little cylindrical tubes. Similarly, formula (18) cannot be applied here; for in a wide tube the liquid surface will only be drawn up at the walls, and will remain almost flat in the centre, as shown in outline in Fig. 11. But in reality the surface tension does not carry a liquid column, but a liquid volume $\Delta V$, or, better, a liquid weight $\Delta V \cdot \gamma$. With tubes this $\Delta V$ is given by the formula:

$$\Delta V = \pi \cdot r^2 \cdot \Delta h \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and herein $\Delta h$ is not measured up to the lower limit of the meniscus, but up to a point elevated a little above it, giving an ideal liquid surface, if the

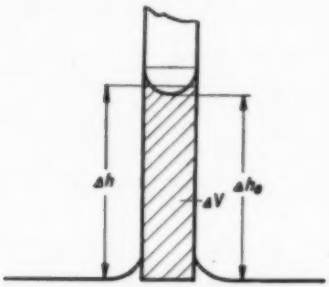



FIG. 10.

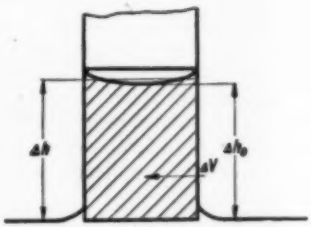



FIG. 11.

meniscus be levelled. $\Delta V$, carried by surface tension, may be calculated by equations (18) and (19) thus:

$$\Delta V = \frac{2 \cdot \alpha \cdot \pi \cdot r}{\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and if this $\Delta V$ is accumulated at the walls, then the surface must be lowered by

$$\Delta h = \frac{V}{r^2 \cdot \pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Then equation (18) is valid for the calculation of the elevation of the meniscus on account of surface tension for all kinds of cylindrical vessels. It can easily be seen that the amounts by which the level is lowered become rapidly very small with increasing $r$.

That is not the case with sloping walls or with curved walls; the upper

Fig. 10. With tubes up to a diameter of 0·2 cm. the surface looks like a hemisphere. Then the real height of rising $\Delta h$ is found, when $\frac{r}{3}$ is added to the rising height $\Delta h_0$ measured up to the meniscus. With tubes from a diameter of 0·2 cm. up to 0·8 cm., the surface has the form of a rotation ellipsoid, and the correction $\Delta h - h_0$ then amounts to $\frac{2\alpha r}{6\alpha + r^2\rho}$ ($\rho$ = spec. density) (see Kohlrausch: "Handbook of Practical Physics," Berlin, 1935).

vessel of our viscometer is ball-shaped. The liquid is drawn up at the walls of this vessel in the direction of the tangent of the sphere, and in a vertical direction only the part $\alpha \cdot \cos\delta$ is active. The amount of liquid, supported by this part of $\alpha$, may then be calculated in accordance with the above from:

$$2\pi \cdot r \cdot \cos\delta \cdot \alpha = \pi \cdot r^2 \cdot \Delta h \cdot \gamma \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Fig. 12 shows that

$$\cos\delta = \frac{r}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and with equation (23) equation (22) gives the relation

$$\Delta h = \frac{2 \cdot \alpha}{\gamma \cdot R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

But with this relation a change of pressure head on account of surface tension becomes also a function of $\alpha$ and $\gamma$, as in equation (18), and of the radius $R$ of the ball.*

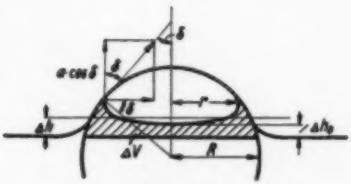



FIG. 12.

Having studied the influence of surface tension in the upper parts of a viscometer, we may now calculate the total influence of surface tension on the measurement, which depends also on the time during which the liquid remains in the different parts of the viscometer.

For this purpose we take equation (1)

$$V = t \cdot \frac{\pi \cdot g \cdot h \cdot r^4}{8 \cdot l \cdot \nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and for the sake of simplicity we introduce $\frac{\pi \cdot g \cdot r^4}{8 \cdot l \cdot \nu} = C_4$

then:

$$V = C_4 \cdot t \cdot h \cdot \frac{1}{\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Now we divide this volume $V$ into the volume $V_2$, contained in the cylindrical tubes of the upper vessel and the volume $V_1$ in the upper ball (see Fig. 13). Then with these parts of the volume parts of the time of discharge

* This is quite valid only for such small rises that the flexure of the sphere may be neglected as unessential. That is not the case if $r$ is small. But then the vertical component of the surface tension is also very small. Moreover, the real shape of the liquid surface in the ball is not known, and therefore, up to now, an accurate calculation from point to point is not possible. It is therefore assumed that the above relation is a close approximation.

$t_1$ and $t_2$ correspond, and for liquids with the same kinematic viscosity there is

$$t_1 \cdot \frac{h_1}{V_1} = t_2 \frac{h_2}{V_2} = t \cdot \frac{h}{V} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

if $h_1$ is the pressure head corresponding with the volume in the ball, and $h_2$ the pressure head corresponding with the volume in the tubes. Furthermore, there is:

$$V_1 + V_2 = V; \quad t_1 + t_2 = t \cdot \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Then with (25) we have:

$$V_1 = \frac{C_4}{\nu} \cdot t_1 \cdot h_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28a)$$

$$V_2 = \frac{C_4}{\nu} \cdot t_2 \cdot h_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28b)$$

and together with equation (27) we find

$$V = V_1 + V_2 = \frac{C_4}{\nu} \cdot (t_1 \cdot h_1 + t_2 \cdot h_2) \quad . \quad . \quad . \quad (29)$$

The corresponding pressure heads are found by subtracting corresponding values on account of surface tension from an absolute average pressure head. In the first, we will call these values $\Delta h_1$ and $\Delta h_2$, so that

$$h_1 = h - \Delta h_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30a)$$

$$h_2 = h - \Delta h_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30b)$$

Then with equation (29) we find

$$V = \frac{C_4}{\nu} \cdot \{t_1 \cdot (h - \Delta h_1) + t_2 \cdot (h - \Delta h_2)\}$$

$$= \frac{C_4}{\nu} \cdot \{h \cdot (t_1 + t_2) + (t_1 \cdot \Delta h_1 + t_2 \cdot \Delta h_2)\} \quad . \quad . \quad (31)$$

Then, together with equation (27):

$$\frac{\nu \cdot V}{C_4} = h \cdot t - t_1 \cdot \Delta h_1 - t_2 \cdot \Delta h_2 \quad . \quad . \quad . \quad . \quad (32)$$

Equations (26) and (30) give:

$$t_1 = \frac{h \cdot V_1}{V \cdot h_1} \cdot t = t \cdot \frac{h \cdot V_1}{V \cdot (h - \Delta h_1)}$$

$$t_2 = t \cdot \frac{h \cdot V_2}{V \cdot h_2} = t \cdot \frac{h \cdot V_2}{V \cdot (h - \Delta h_2)}$$

We insert these values in equation (32) and find

$$\frac{\nu \cdot V}{C_4} = h \cdot t - t \cdot \frac{h \cdot V_1}{V \cdot (h - \Delta h_1)} - t \cdot \frac{h \cdot V_2}{V \cdot (h - \Delta h_2)}$$

$$= t \cdot \left\{h - \frac{h}{V}\left(\frac{V_1 \cdot h_1}{h - \Delta h_1} + \frac{V_2 \cdot h_2}{h - \Delta h_2}\right)\right\} \cdot \quad . \quad . \quad . \quad . \quad (33)$$

Furthermore, with equation (18), we have:

$$h_2 = \frac{2 \cdot \alpha}{R_2 \cdot \gamma}$$

and with equation (24):

$$h_1 = \frac{2 \cdot \alpha}{R_1 \cdot \gamma}$$

and inserting these values in equation (33) we find:

$$\frac{\nu \cdot V}{C_4} = t \cdot \left\{ h - \frac{h}{V} \cdot \left( \frac{V_1 \cdot \frac{2 \cdot \alpha}{\gamma \cdot R_1}}{h - \frac{2 \cdot \alpha}{\gamma \cdot R_1}} + \frac{V_2 \cdot \frac{2 \cdot \alpha}{\gamma \cdot R_2}}{h - \frac{2 \cdot \alpha}{\gamma \cdot R_2}} \right) \right\}$$

$$= t \cdot \left\{ h - \frac{2 \cdot \alpha}{\gamma} \cdot \frac{h}{V} \left( \frac{V_1}{R_1 h - 2\alpha/\gamma} + \frac{V_2}{R_2 h - 2\alpha/\gamma} \right) \right\} \quad . \quad . \quad (34)$$

The relation (34), so found, is the equation (1), corrected on account of surface tension. It differs from equation (1) only by a diminished value of $h$. The value to be subtracted from $h$ is determined by the surface tension of the liquid tested, by its specific gravity, by the divided volume and the radii corresponding to the parts of the volume.

If, moreover, equation (34) shows that the influence of surface tension is merely a decrease of the effective pressure head, it must be possible to eliminate this influence by an opposing traction of surface tension, directed vertically downward. That is possible: if we choose the lower level of the viscometer in the form of a hemisphere—for example, with the radius $R_0$—then the surface tension pulls downward in this level with a value $\Delta h = \frac{2 \cdot \alpha}{\gamma \cdot R_0}$, as shown by equation (24). Then it must be possible to choose the radius $R_0$ so that the traction action $\Delta h$, caused by this level, is just equal to the correction of $h$ in equation (34), but with the opposite sign.

To be explicit, we repeat the calculation. At first here, too, the discharged volume is divided into the parts $V_1$ and $V_2$ corresponding to the volume in the ball and the volume in the adhering tubes. Further, the time of flow is divided in corresponding parts $t_1$ and $t_2$, and corresponding average heads $h_1$ and $h_2$ are assumed (see Fig. 13). From $h_1$ and $h_2$ we find the absolute average pressure head, if we subtract the traction of surface tension at the lower level and add the corresponding traction at the upper surface, so that:

$$h_1 = h + \frac{2 \cdot \alpha}{\gamma \cdot R_0} - \frac{2 \cdot \alpha}{\gamma \cdot R_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (35a)$$

$$h_2 = h + \frac{2 \cdot \alpha}{\gamma \cdot R_0} - \frac{2 \cdot \alpha}{\gamma \cdot R_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (35b)$$

From equation (32) we find then:

$$t_1 = \frac{t \cdot h \cdot V_1}{V \cdot \left( h + \frac{2 \cdot \alpha}{\gamma \cdot R_0} - \frac{2 \cdot \alpha}{\gamma \cdot R_1} \right)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

and with equation (27) this gives:

$$t_2 = t - t_1 = \frac{t \cdot h \cdot V_2}{V \cdot \left(h + \frac{2 \cdot \alpha}{\gamma \cdot R_0} - \frac{2 \cdot \alpha}{\gamma \cdot R_2}\right)} \quad . \quad . \quad . \quad (37)$$

Then the sum $t_1 + t_2 = t$ is obtained

$$t = \frac{t \cdot h}{V} \cdot \left( \frac{V_1}{h + \frac{2 \cdot \alpha}{\gamma \cdot R_0} - \frac{2 \cdot \alpha}{\gamma \cdot R_1}} + \frac{V_2}{h + \frac{2 \cdot \alpha}{\gamma \cdot R_0} - \frac{2 \cdot \alpha}{\gamma \cdot R_2}} \right) \cdot \quad . \quad (38)$$

If we divide by $t$, we find an equation which gives a relation between $R_0$ and $\alpha$:

$$1 - \frac{V_1}{V} \cdot \frac{h}{h + \frac{2 \cdot \alpha}{\gamma} \cdot \left(\frac{1}{R_0} - \frac{1}{R_1}\right)} = \frac{V_2}{V} \cdot \frac{h}{h + \frac{2 \cdot \alpha}{\gamma} \cdot \left(\frac{1}{R_0} - \frac{1}{R_2}\right)} \quad . \quad . \quad (39)$$

This relation is a quadratic for $\left(\frac{1}{R_0}\right)^2$ and $\frac{1}{R_0}$, and with it $R_0$ may be calculated from equation (39). So we find, if at the same time introducing for the specific weight $\gamma$, specific density $\rho$.

$$\frac{\alpha}{\rho} \cdot \frac{1}{R_0^2} + \frac{1}{R_0} \left\{ \frac{h \cdot g}{2} - \left(\frac{R_1 + R_2}{R_1 \cdot R_2}\right) \cdot \frac{\alpha}{\rho} \right\} - \left\{ \frac{h \cdot g}{2} \left( \frac{V_1}{V} \cdot \frac{1}{R_1} + \frac{V_2}{V} \cdot \frac{1}{R_2} \right) - \frac{1}{R_1 \cdot R_2} \cdot \frac{\alpha}{\rho} \right\} = 0 \quad . \quad . \quad (40)$$

From equation (40) we now see that the influence of surface tension cannot be eliminated once for all, as it would seem at first. In fact, for every value of $\frac{\alpha}{\rho}$ a specific value of the radius of flexure $R_0$ at the lower level is necessary; all other measurements of the viscometer remaining unaltered. In practice, however, values of $\frac{\alpha}{\rho}$ in the limits of 0 and 100 only are known, and we will show later, that for these values practically only one radius of curvature $R_0$ is valid.

But first let us sum up our results so far:

1. The suspended level, flat and curved, guarantees the formation of a hanging layer at the same elevation for all liquids of whatever kind, independent of their kinetic energy, their specific gravity and other properties.

2. In using the flat level, every action of surface tension at the lower level is automatically eliminated.*

3. In using a spherical level, such a traction of surface tension can be caused at the lower level that it equals the traction of the surface tension at the upper meniscus in an opposite direction, and therefore no correction on account of surface tension is necessary.

* This fact renders the flat level very useful for a new type of apparatus for determination of surface tension by the rise of a liquid within a capillary, as already described in our paper of May 1933 mentioned above.

## III. Experiments on the Elimination of the Traction of Surface Tension at the Upper Surface by the Tractive Action of the Suspended Spherical Level.

To investigate the influence of surface tension, we used viscometers with suspended levels. Within the limits of the Poiseuille formula, there is for a so-called " relative viscometer "

$$= t \,.\, k \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

wherein $k$ is the calibration constant of the apparatus, with the value

$$k = \frac{\pi \,.\, g \,.\, h \,.\, r^4}{8 \,.\, l \,.\, V}$$

Naturally, the numerical value of such a calibration constant can only be given if the values of which it is composed are constant. That is the case for $r$ and $l$, and with the same temperature also for $V$ with reasonable accuracy. Moreover, as we have shown by calculation and by experiment,* the suspended level guarantees the automatic formation of the same average distance of elevation between the liquid levels.

With the suspended level at a plane annular surface there is no tractive action of surface tension at the lower level. However, the surface tension at the upper meniscus bears an amount of liquid which has to be subtracted from the effective average head. If, therefore, we calibrate our viscometers with plane suspended level with a liquid of known kinematic viscosity, then the calibration constant so found is valid only for liquids with the same surface tension, or at least almost the same surface tension. For all other liquids we have a correction, relatively small, which may be calculated from the correction of $h$ from equation (33). If, for sake of simplicity, we call this correction of $h$ from equation (33), $K$, then the absolute calibration constant of a viscometer is :

$$k = k_1(h - K) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

and the real kinematic viscosity of a liquid tested in this viscometer :

$$\nu = t \,.\, k_1(h - K) \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

If we determine the viscosities $\nu_1$ and $\nu_2$ of two liquids with different surface tensions, two different corrections of $h$, $K_1$ and $K_2$, corresponding to the surface tensions of the different liquids, then :

$$\nu_1 = t_1 \,.\, k_1(h - K_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (44a)$$

and

$$\nu_2 = t_2 \,.\, k_2(h - K_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (44b)$$

if $t_1$ and $t_2$ are the corresponding times of flow. If we take the ratio between the two viscosities, we find that the times of flow are not directly proportional to the viscosities, but must be corrected by a factor containing the surface tension of the liquid tested, its density and the dimensions of the viscometer.

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* Test data regarding the formation of the suspended level at the same elevation for all kinds of liquids are given in our paper of May 1933. Therefore it was not necessary to repeat them here.

With the spheric level, the tractive action of surface tension will be the same at the lower and at the upper levels. Then $K = 0$.

Therefore, in a viscometer with spheric level, the radius of curvature being calculated from equation (40), the time of flow for two liquids with different surface tensions must correspond directly to the viscosities of the liquids.

Equation (40), however, has shown that every value of $\frac{\alpha}{\rho}$ requires a special value of radius of curvature. We will now give an idea of the numerical values of these radii of curvature.

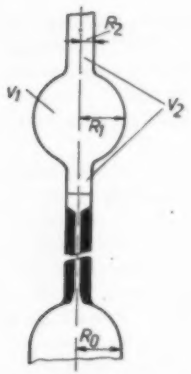


FIG. 13.

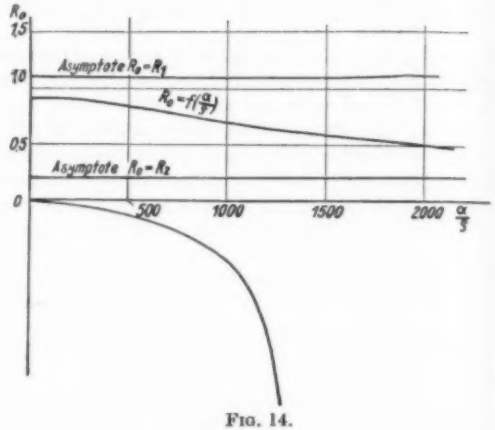


FIG. 14.

With our viscometers, the following average values can be inserted in equation (40) (see also Fig. 13):

$R_1 = 1{\cdot}1$ cm. (radius of the upper ball).
$R_2 = 0{\cdot}2$ cm. (radius of the tubes, connected with this ball).
$l_2 = 2{\cdot}0$ cm. (total length of the tubes at the upper ball).
$h = 13{\cdot}0$ cm. (average absolute pressure head).
$g = 981$ cm. sec.$^{-2}$ (acceleration of gravity).
$V_1 = 5{\cdot}575$ cm.$^3$ (volume of liquid in the ball).
$V_2 = 0{\cdot}251$ cm.$^3$ (volume of liquid in the tubes).
$V = V_1 + V_2 = 5{\cdot}826$ cm.$^3$ (total volume).

With these numbers equation (40) gives

$$\frac{\alpha}{\rho} \cdot \left(\frac{1}{R_0}\right)^2 + \frac{1}{R_0}\left(6376{\cdot}5 - 5909\frac{\alpha}{\rho}\right) - \left(6920{\cdot}66 - 4545\frac{\alpha}{\rho}\right) = 0 \quad . \quad . \quad (45)$$

Then:

$$\left(\frac{1}{R_0}\right)_{1\cdot2} = \frac{2 \cdot \rho}{\alpha}\left\{-\left(6376{\cdot}5 - 5909\frac{\alpha}{\rho}\right) \pm \sqrt{\left(6376{\cdot}5 - 5909\frac{\alpha}{\rho}\right)^2 + \frac{4 \cdot \alpha}{\rho}\left(6920{\cdot}66 - 4545\frac{\alpha}{\rho}\right)}\right\} \quad . \quad . \quad (46)$$

This relation is shown in the curves of Fig. 14. The two hyperbolic parts of the curve outside the asymptotes $R_0 = R_2$ and $R_0 = R_1$ have no technical interest. But the part between the horizontal asymptotes gives all radii of curvature for all values of $\frac{\alpha}{\rho}$. So we find that in the practically possible interval for $\frac{\alpha}{\rho}$ between 0 and 100 the value hardly differs from the value for $\frac{\alpha}{\rho} = 0$. But then equation (40) may be simplified by assuming $\frac{\alpha}{\rho} = 0$. Thus we arrive at a form for practical calculation:

$$\frac{1}{R_0} = \frac{V_1}{V \cdot R_1} \pm \frac{V_2}{V \cdot R_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

which gives $R_0$ for all values of $V_1$ and $V_2$ and corresponding values of $R_1$ and $R_2$ with quite sufficient accuracy. From equation (47) we may calculate $R_0$ with the numbers given above and find for our viscometer $R_0 = 0{\cdot}921$ cm. If we insert $\frac{\alpha}{\rho} = 100$ in equation (46), we find $R_0 = 0{\cdot}9175$, so that the decrease in $R_0$ is in fact very small, if $\frac{\alpha}{\rho}$ increases from 0 to 100, and we can assume $R_0 = 0{\cdot}92$ cm. for all liquids without any considerable error.

To test the accuracy of our calculation, we have determined the time of flow of benzene and of water in several viscometers with spheric level with a radius of curvature $R_0 = 0{\cdot}92$ cm. As the values of the kinematic viscosity of benzene differ widely in literature, we determined the corresponding times of flow also in a series of viscometers with plane level. Then, assuming the kinematic viscosity of water as correct,* we calculated the kinematic viscosity of benzene by these times of flow.

But, before giving the test data and the calculations derived from them, something may be said about the method of making the test.

First, to eliminate even the slightest error in temperature, in all experiments a constant temperature bath was used; this allowed adjustment of the temperature to $20° \pm 0{\cdot}001°$ C. for any required time.

Before use the viscometers were filled with dilute chromosulphuric acid (when concentrated, it attacks glass), warmed some time to 80–90° C. and then thoroughly rinsed out with distilled water. They were then rinsed out several times with alcohol and finally dried completely under vacuum. This operation of cleaning was repeated before every new filling. The last liquids for cleaning, as well as the liquids to be tested, are filtered through a filter of fritted Jena Glass G4. Furthermore, before making the test, the viscometers were rinsed out with the fluid to be tested.

The passing of the liquid meniscus through the marks was observed by telescope and scale. The time of flow was measured with two stop-watches simultaneously. (These were exchanged regularly between the hands of the operator.) The difference between the watches was, in a test of 30 minutes, on an average less than 0·25 second.

* According to measurements by Bingham and White, see Landolt-Börnstein, *Phys. chem. Tabellen.*

Thus times of flow for benzene and water were obtained in five viscometers with plane level, so that three new fillings were made, and with every filling the time of flow was determined seven times. The average from these seven times of flow was then taken, and once more the average from the three average values. Thus were found the values given in Table I.

TABLE I.

| No. of the Viscometer. | Time of Flow of Water, seconds. | Maximum Average Error, %. | Time of Flow of Benzene, seconds. | Maximum Average Error, %. |
|---|---|---|---|---|
| 1 | 106·0 | 0·03 | 77·6 | 0·03 |
| 2 | 103·7 | 0·03 | 76·8 | 0·00 |
| 3 | 105·6 | 0·03 | 78·1 | 0·00 |
| 4 | 98·3 | 0·02 | 73·0 | 0·03 |
| 5 | 104·5 | 0·03 | 77·3 | 0·03 |

For calculating the kinematic viscosity of benzene from these values the effective pressure heads must be corrected because of surface tension. The pressure head can be calculated from the time of flow for water.

The upper balls of our viscometer are manufactured by the glass-blower by enamelling before the lamp. To discover how these balls differ in volume from the values assumed for the calculation of the spheric level, five balls, filled with water between the marks at a temperature of 23·5° C., were weighed.

The weights are the average of seven single weighings, and the balls had an average volume of 5·671 cm.$^3$. In the departures from the average value we found an average error of 0·1 per cent. maximum. Only a small difference exists as compared with the value given for calculation above. But in our further calculations, the volume thus obtained 5·671 cm.$^3$ will be used. The length of the capillary also was measured in a series of viscometers, and on an average it was found to be $l = 9{\cdot}09$ cm., with an average error of 0·35 per cent.

Equation (1) may be substituted by

$$\nu = t \cdot \frac{\pi \cdot g \cdot h \cdot r^4}{8 \cdot l \cdot V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

and with $\frac{\pi \cdot g \cdot r^4}{8 \cdot l \cdot V} = C_5$ we find:

$$\nu = t \cdot h \cdot C_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

From this equation the pressure head can be found

$$h = \frac{\nu}{C_5 \cdot t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

If we calculated $C_5$ with the values given above for $r$, $l$ and $V$, we introduce an error, on account of the fact that there are small errors in $V$ and $l$. But these errors will certainly not amount to more than 0·3 per cent. Then $C_5 = 7{\cdot}65 \cdot 10^{-6}$. For the kinematic viscosity of water (several times distilled and thoroughly freed from air before testing) 1·007 centistokes (calculated from $\eta = 1{\cdot}0043$) is to-day regarded as the most correct

value.* Then from the times of flow for water the corresponding pressure heads given in col. 1 of Table II are found.

The correction to be applied to these pressure heads on account of surface tension is found from equation (34) to be:

$$-\frac{2 \cdot \alpha}{\gamma \cdot V}\left(\frac{V_1}{R_1 h - 2\alpha/\gamma} + \frac{V_2}{R_2 h - 2\alpha/\gamma}\right)$$

Therefore it is necessary to divide the volume found by weighing out the balls in the part-volumes $V_1$ and $V_2$. (But this is possible only by introducing a further slight error, because the diameter of the tubes connected with the upper bulb differs slightly between the values 0·35 and 0·4 cm. Furthermore, the upper vessel, being formed by enamelling before the lamp, is not accurately spherical in shape.†)

The distance between the ball and the marks is generally less than 0·5 cm. With a radius of the tubes of 0·2 cm. the volume $V_2$ then is 0·126 cm.$^3$, and with $V = 5{\cdot}671$ cm.$^3$ $V_1$ it is found to be 5·645 cm.$^3$, corresponding to a ball with radius 1·097 cm. These values will be the best average values for the viscometers as used (and an error will only be small when general calculations are based on these values).

On the right-hand side of equation (34) there is a product of $t$ and a pressure head corrected on account of surface tension. Consequently in determining the time of flow of a liquid with known kinematic viscosity in a viscometer, and calculating the pressure head from this time of flow, the factor of $t$ on the right-hand side of equation (34) is found. Thus a cubic equation for $h$ is formed, the solution of which must result in the true average head $h$, unaffected by surface tension. But in attempting the calculation, it will soon be found that even the small errors and differences in the values for $V_1$ and $V_2$, $R_1$ and $R_2$, and even $\alpha$, by squaring and cubing, become big enough to cause considerable errors in results. Moreover, the numerical calculation of the cubic equation being very difficult, a graphic solution is preferred. For this purpose the value of the correction for average heads between 12 and 14 cm. in steps of 0·1 cm. and for values of surface tension up to 90 dyn. cm.$^{-1}$ were calculated. These values we have plotted on a diagram, which has as ordinates the average heads and as abscissæ the values of $\frac{\alpha}{\rho}$. We thus obtain a series of curves as shown in Fig. 15, the curves beginning for the value of $\frac{\alpha}{\rho} = 0$ with the uncorrected average head and falling with a very slight flexure to the corrected values. Thus it is possible to read from this diagram true average pressure heads corresponding to calculated figures that are subject to surface tension influences.

From this diagram, with a surface tension of water 72·72 dyn. . cm.$^{-1}$ at 20°,‡ the true average pressure heads of our viscometers given in col. 3 of

* See footnote, p. 443.

† But having found that even very small deviations in the upper ball and the tubes connected with it are of importance when the last causes of error are to be eliminated, in future tubes of the same diameter and balls of a real spherical shape will be used in the manufacture of the viscometers.

‡ According to measurements of *Sugden* and of *Harkis* and *Brown*, see footnote, p. 443.

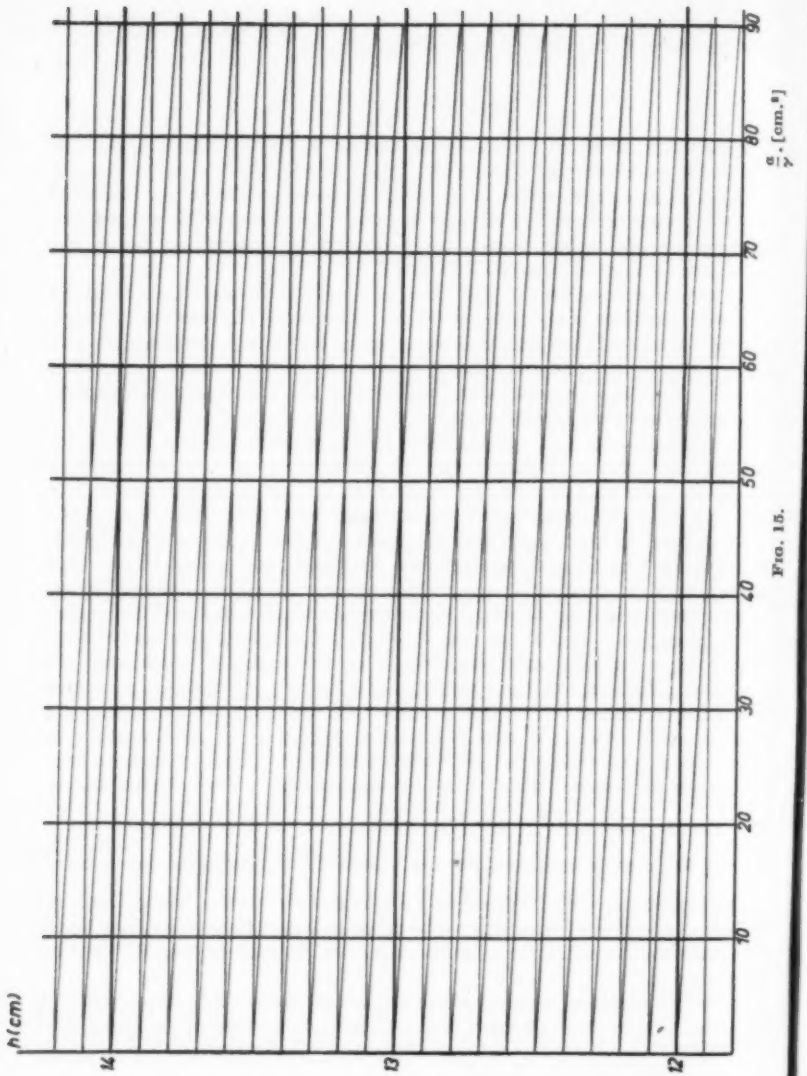


FIG. 15.

Table II and the corresponding pressure heads for benzene given in col. 4 of Table II can be read. With these values the times of flow of benzene, corresponding to the absolute average heads, are found as the values given in col. 5 of Table II. From these times of flow the viscosity of the benzene

TABLE II.

| No. of Viscometer. | Average Head Calculated from Time of Flow of Water. | Real Average Head. | Average Head for Benzene. | Time of Flow of Benzene Corrected to Real Average Head. | Viscosity of Benzene in *cSt.* |
|---|---|---|---|---|---|
| 1 | 12·5 | 12·5 | 12·58 | 78·05 | 0·7625 |
| 2 | 12·65 | 12·80 | 12·73 | 77·2 | 0·7630 |
| 3 | 12·43 | 12·58 | 12·51 | 78·55 | 0·7630 |
| 4 | 13·35 | 13·50 | 13·43 | 73·40 | 0·7650 |
| 5 | 12·56 | 12·71 | 12·64 | 77·7 | 0·7625 |

used (supplied by Kahlbaum-Schering, purest, crystallized) is shown by the values of col. 5 in Table II. Herein the surface tension of benzene was taken as 28·9 dyn. . cm.$^{-1}$ * and its specific gravity as 0·87865.†

Then the average viscosity of benzene is 0·7632 centistokes, ‡ the mean error of this average value being 0·8 per cent.

Omitting the value 4 in the calculation of the average values, this being subject to correction on account of kinetic energy (the average head being far greater than the others), then the viscosity of benzene would display an average error which is smaller by nearly a power of ten. But we will at first retain the error of 0·8 per cent. in the average value of the viscosity of benzene.

Theory now requires that the ratio between the times of flow in the viscometer with spheric level is equal to the ratio between the viscosities of the liquids tested. Therefore the times of flow were determined in a series of viscometers with spheric level of a radius of curvature 0·92 cm. in the

TABLE III.

| No. of the Viscometer. | *t* of Benzene. | *t* of Water. | Average Ratio between Times of Flow. |
|---|---|---|---|
| 6 | 77·2 | 104·0 | 0·7425 |
| 7 | 76·3 | 102·8 | 0·7425 |
| 8 | 76·4 | 103·0 | 0·7420 |
| 9 | 77·1 | 103·6 | 0·7440 |
| 10 | 77·2 | 103·8 | 0·7435 |

same way as in the viscometers with plain level—that is, with three fillings every time, seven times of flow were determined and from the times of flow the average value was taken. So the values of Table III are found.

* According to *Richards* and *Harkis* and *Brown*, see footnote, p. 443.

† According to *Biron*, see footnote, p. 443.

‡ This is not the absolute kinematic viscosity of benzene, on account of the fact that correction for kinematic energy was not considered, the times of flow being almost the same in the viscometers with spheric level.

FIG. 15.

From the values of col. 3 of Table III the average ratio between the times of flow is found to 0·7429 and from the viscosities of benzene and water the theoretical value 0·7495 is found. Therefore, as compared with theory, there is a difference of only 0·0066. And if it be considered that there are differences in $R_2$, and therefore errors in $V_2$, and that the upper vessel had not yet the shape of a sphere, then such close agreement may, without doubt, be taken as good proof of the accuracy of the calculations and deductions.

Moreover, this difference is due only to a small deviation in the correction for surface tension. But this correction amounts to only 1 per cent. of the pressure head, and causes only a change in time of flow which is almost two powers of ten smaller. Thus with the above difference we have reached the limits of our possible measurements.

## IV. Description of the Apparatus Used and the Correction Table for Kinetic Energy.

Fig. 16 gives a diagrammatic view of the viscometer.

To the pipette-like bulb $A$, with marks $m_1$ and $m_2$, is attached at the bottom the capillary 4, which leads to a cylindrical vessel $C$ about 12 mm. in diameter. The lower end of the capillary is tapered to a funnel shape, and

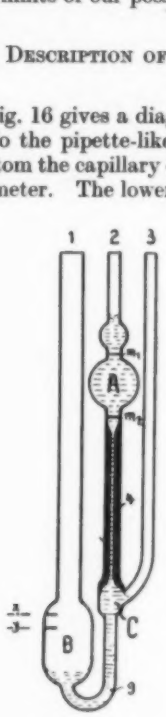


Fig. 16.

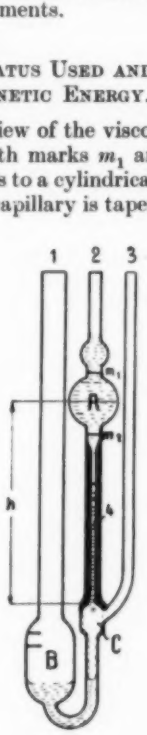


Fig. 17.

Fig. 18.

its emergence to the vessel $C$ has the form of a hollow hemisphere. After the vessel $C$ comes a curved tube $g$, and then the lower bulb $B$. This is connected with the atmosphere through a large tube 1, while the bulb $C$ is connected through tube 3.

If bulb $B$ is filled with liquid through tube 1 until the meniscus lies between the marks $x$ and $y$ and vacuum is applied by means of a rubber

tube, placed on tube 2, while tube 3 is kept closed at the top with the finger, then the bulb $C$, the capillary 4 and the bulb $A$ are filled in succession, so that the condition is reached which is shown in Fig. 16. If then tubes 2 and 3 are opened, air enters bulb $C$ through tube 3, the liquid is immediately divided into two parts, and the condition is brought about which is shown by Fig. 17. Furthermore, a thin liquid layer is immediately formed in the hollow hemisphere, at the end of capillary 4, in which is located the "suspended level," with a free surface facing downward. This liquid layer lies at the same elevation for all liquids which wet the surface. Simultaneously with the formation of the suspended level the liquid begins to flow out of the bulb $A$ through the capillary; however, it does not refill the bulb $C$, but flows down in a thin layer on the vertical wall of the vessel, and joins the liquid in $g$ and $B$. The observer has only to determine the time in seconds in which the liquid meniscus falls from the mark $m_1$ to the mark $m_2$, the method of operation being thus as simple as possible.

The apparatus as used in Fig. 18 is similar to that shown diagrammatically in Fig. 16, but it is more compact because tubes 1, 2 and 3 are arranged in a triangle with respect to one another; furthermore, the glass instrument is enclosed in a frame, consisting of two round end-pieces and three rods, so that it is protected.

The capillaries are supplied with three calibration constants, 0·01, 0·1 and 1·0. That was possible on account of the fact that the average head in these viscometers is constant and all other measurements can be adjusted

TABLE IV.

CORRECTION TABLE (TO CORRECT FOR KINETIC ENERGY).

| Observed Time of Flow, secs. | Correction in Seconds for Capillary. | | |
|---|---|---|---|
| | I. | II. | III. |
| 20 | (14·1) | (1·41) | *0·14* |
| 25 | (11·2) | (1·12) | *0·11* |
| 30 | (9·34) | (0·93) | *0·1* |
| 35 | (8·1) | 0·81 | *0·08* |
| 40 | (7·0) | 0·7 | *0·07* |
| 45 | (6·27) | *0·63* | *0·06* |
| 50 | (5·6) | *0·56* | *0·06* |
| 55 | (5·1) | *0·51* | *0·05* |
| 60 | (4·68) | *0·47* | *0·05* |
| 70 | (4·01) | *0·41* | *0·04* |
| 80 | 3·5 | *0·35* | *0·04* |
| 90 | 3·1 | *0·31* | *0·03* |
| 100 | 2·8 | *0·28* | *0·03* |
| 120 | 2·34 | *0·23* | *0·02* |
| 140 | 2·00 | *0·2* | *0·02* |
| 160 | 1·75 | *0·175* | *0·02* |
| 180 | 1·56 | *0·16* | *0·02* |
| 200 | 1·4 | *0·14* | *0·01* |
| 250 | 1·12 | *0·11* | *0·01* |
| 300 | 0·94 | *0·09* | |
| 350 | 0·80 | *0·08* | |
| 400 | 0·70 | *0·07* | |
| 450 | 0·63 | *0·06* | |
| 500 | 0·56 | *0·06* | |

to it. But for special cases also capillaries with calibration constants 0·006, 0·05, 0·5, 5·0 and 10·0 may be supplied.

The calibration constants being powers of ten in the usual form of the viscometer, the determination of the kinematic viscosity from the time of flow is easy, because only a decimal point has to be placed in the time of flow.

Table IV, corrections on account of kinetic energy, is calculated for the capillaries with powers of ten as calibration constants. But the values for the other calibration constants may easily be found by linear interpolating between the values in the table, which are also valid, if the calibration constant is not quite a power of ten. The designation I, II and III corresponds to the calibration constants 0·01, 0·1 and 1·0. With the values in parentheses, the correction may be erroneous to 7 per cent. But with values underlined, the error will be less than 0·1 per cent., and the time of flow should be chosen so that only such values are used.*

It may be mentioned that some liquids easily form bubbles in the vessel $C$ if air should enter through tube 3. These bubbles must be eliminated before conducting the test, which may easily be done by keeping the tubes 1 and 2 closed at the top with the finger and applying vacuum to tube 3 for a short time. When air re-enters, the bubbles will burst immediately.†

## V. Summary.

The new *suspended level* principle was applied to viscometers and a new type of viscometer was designed which has the suspended level in place of the usual lower liquid surface. Thus by its aid viscometers are freed from previously unavoidable errors in the adjustment of the lower liquid surface, and an instrument has been developed of unsurpassed simplicity and pre-eminent accuracy.

By using a *suspended spheric level*, even correction on account of surface tension could be eliminated.

The difficulty of correction for kinetic energy still remains. This is necessary with all previously known instruments, and yet it has often been neglected, although errors could thence arise of greater magnitude than from other sources, thus rendering the instrument unserviceable; this is obvious when it is appreciated how difficult it is to apply the correction. The next object, therefore, was to eliminate this difficulty, and this was

* Concerning the accuracy of the Table see: Ubbelohde: "Zur Viskosimetrie" ("On the Measurement of Viscosity," 2nd edition, Leipzig (1936)). An English translation of the book is prepared. In former papers and in the first edition of "Zur Viskosimetrie," the table calculated on the value $m = 0{\cdot}8$ was given, because it was found that this resulted in a better correction than when using the value $m = 1{\cdot}12$ from literature. This was due to the fact that the funnel was too small in the former viscometers and it is no longer valid—$m$ is the factor of the Hagenbach-Couette correction to the Poiseuille formula

$$\nu = t\frac{\pi \cdot g \cdot h \cdot r^4}{8 \cdot l \cdot v} - m \cdot \frac{V}{8 \cdot \pi \cdot l \cdot t}$$

† The viscometers are protected by British patent No. 400,840. They are supplied by the Jenaer Glasswerks, Schott and Gen., Jena, Germany, Abt. KaPeG. English agents: C. Myers, 31, Grosvenor Place, London, S.W. 1.

achieved by fixing the value of the correction once for all and making it possible that mere multiplication of the corrected time of discharge by a power of ten (*i.e.* moving the decimal point) is necessary in order to obtain directly the kinematic viscosity in centistokes.

To make the dimensions of the apparatus, especially the capillary, accurate enough, it was necessary to manufacture the capillaries with an accuracy of at least 0·01 mm.

Consideration of all these factors has produced an instrument that is so easy to use and in which all errors are so thoroughly eliminated that in the future it should be scarcely excusable if viscosity data of dubious value are obtained.

I wish to thank my collaborators in this lengthy work—namely, Diploma Engineer Max Kemmler for help in the calculation of the influence of surface tension, Dr. Engineer E. Leibnitz for collaboration in checking the calculations and for conducting the numerical calculations from the text data.

# THE COEFFICIENT OF STATIC FRICTION OF DIFFERENT LUBRICATING OILS MEASURED WITH THE "REDGROVE APPARATUS."

By D. J. W. Kreulen (Member).

## Introduction.

In 1935 E. R. Redgrove (*J.I.P.T.* (1935), **21**, 612) introduced a simple apparatus for testing the "oiliness" of lubricating oils. This apparatus was described by him as follows:

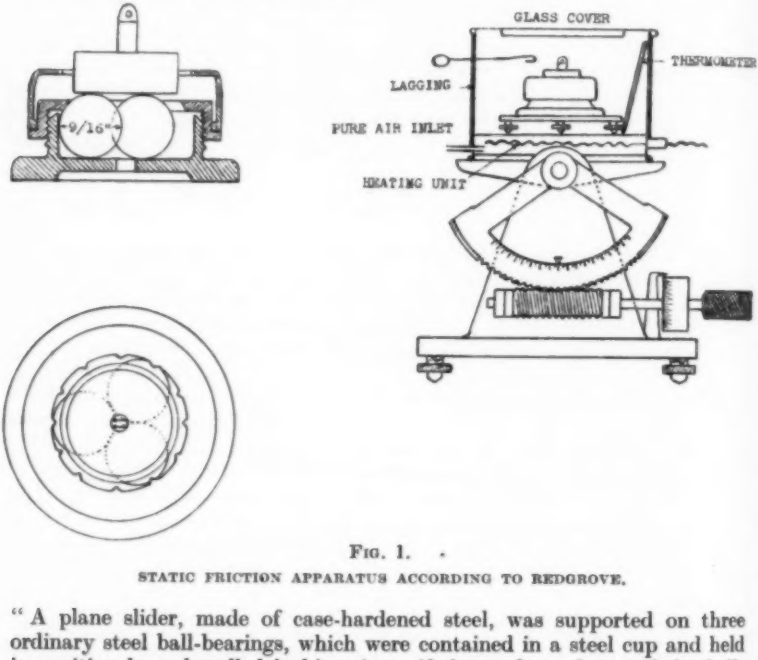


Fig. 1.

STATIC FRICTION APPARATUS ACCORDING TO REDGROVE.

"A plane slider, made of case-hardened steel, was supported on three ordinary steel ball-bearings, which were contained in a steel cup and held in position by a bevelled locking-ring; if the surface of any of the balls became scratched, the locking-ring was released and a fresh surface was presented by slightly rotating the damaged ball. A guard-ring controlled the lateral movement of the slider, preventing it from slipping entirely off the bearing surfaces, and so becoming contaminated. This apparatus was enclosed in a lagged metal box through which a stream of purified and dried air could be passed, and an electric heater was provided. The whole was mounted on a table, which by means of a worm and wheel gearing could be tilted until the angle was attained at which slip of slider occurred."

As the results obtained with this apparatus, which are given in the same paper, suggested that it would be possible to obtain in this simple way valuable information with regard to the " oiliness " of a given lubricating oil, we decided to build a similar apparatus and to test therein lubricating oils of different character. In this paper the results thereby obtained are described.

## Description of Experiments and Results.

Contrary to the experience obtained by Redgrove, serious difficulties were encountered in the beginning with regard to a satisfactory agreement of results, although the prescribed method for preparing and cleaning the surface of the slider was very carefully followed. The surface was lapped with flour of emery mixed with the oil, the coefficient of friction of which it was desired to determine, subsequently thoroughly washed with petroleum ether, then refluxed with pure absolute alcohol, and immediately after the alcohol-film had evaporated the surface was covered with the oil under test. The ball bearings were treated similarly, with the exception of the application of flour of emery.

Thus Redgrove did not work with a polished slider, since it was treated with an oil-emery paste until a matt finish was obtained. We at first did the same, but it was soon realized that if the slider was matt, once slipping it caused scratches on the polished balls. This scratching of the balls, causing a matt plane on each of them, could be easily observed with a magnifying-glass. It resulted in increasing the coefficient of friction in each succeeding test. We attributed the scratching to the high bearing-pressure per surface unit, and proceeded to use a plane-ground piece of metal on which the slider was placed, in order to reduce the bearing-pressure. However, although no scratching then occurred, no reliable results were obtained, so it was decided to employ polished surfaces. The way in which the slider was placed proved to be of considerable importance, this being attributed to the great number of touching-planes of the surfaces employed. This fault can doubtless be eliminated by using only three small touching-planes as employed by Redgrove in his ball-and-slider method.

The experiments with planes showed us that there was another factor which should be eliminated during the measurement of the coefficient of static-friction—namely, the surface-tension. This factor can be eliminated by placing slider and balls under the oil to be tested. We therefore attached a cylinder to the guard-ring of the apparatus and filled the whole cylinder with the oil, so that the balls as well as the slider were entirely covered with the oil under test. The slider was made of hardened carbon tool steel with about 0·7 per cent. of carbon. It was polished with finer and finer amaril until, after the finest amaril (applied dry), a glittering surface was obtained. This surface was further improved by applying a polish (tripel) on a hard polishing-surface. Relief-polishing was avoided as much as possible. This slider was supported on three balls, which were not similarly treated, but left in their natural polished state. Employing these surfaces, the results were such that after some days an end-value was reached which proved to be a repeatable constant of the oil.

The following details can be given concerning the method of carrying out the test. The surface of slider and ball are cleaned as carefully as possible. The directions as given by Redgrove, eliminating the flour of emery treatment, may be followed and a final reflux with pentane is recommended. After filling the apparatus with the oil, the slider is placed in position, and every 10 minutes a slip-test is made, one after the other to the

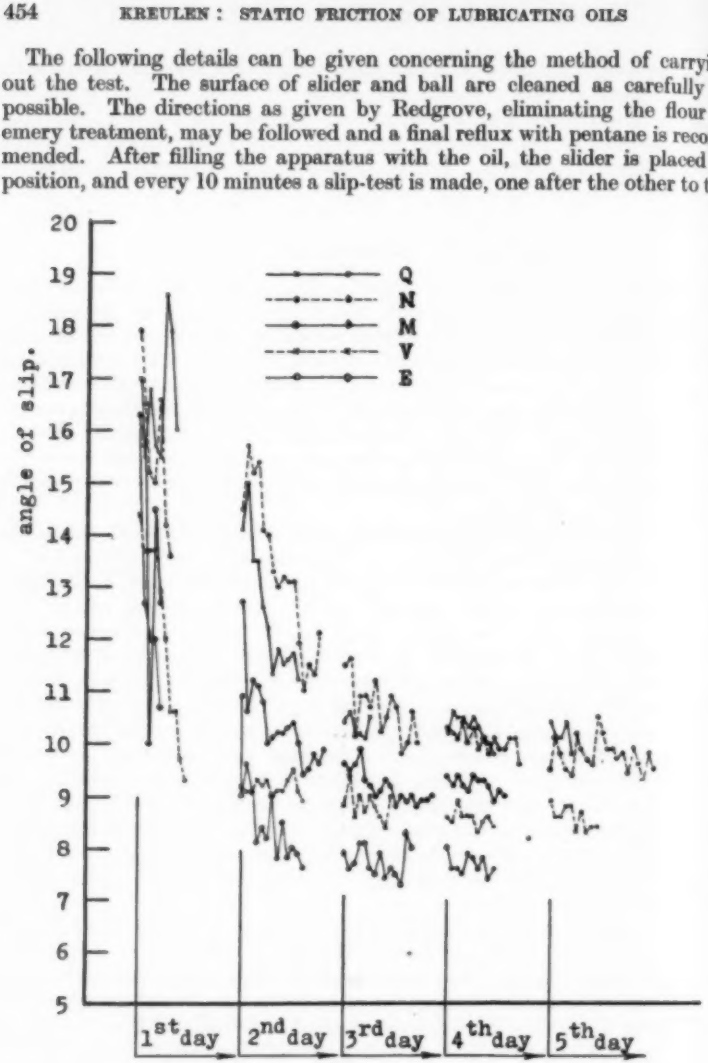


FIG. 2.

left and to the right. Two successive tests (one to the left and the following to the right) are averaged, the resulting value being indicated in a graph as a function of time.

The tests were carried out at room temperature. As it was winter, the temperature of the room was so regulated that the tests must have been carried out at 20° ± 2° C. In Fig. 2 a graph is given in which the results obtained for five different oils are compared.

Each point in the graph is also the mean of a measurement to the right and to the left. It is seen from this graph that the equilibrium is very slowly attained—in most cases a complete test requires 4 to 5 days. After this time, however, a certain end-value is reached which fluctuates round a definite mean value. It is the tangent of this mean angle which is called the coefficient of static friction. The test is ended if the mean tangent does not fluctuate more than 2 units in the third decimal in two successive days.

The fact that the equilibrium establishes itself so slowly is not astonishing, as we are here concerned with a physical process. It would certainly be more surprising if the end-value was reached at once.

The coefficient of static friction was determined for seven oils, five of which were mineral oils, the constants of which are collected in Table I.

TABLE I.

| Oil. | Conradson. | Viscosity c.st. 37·8° C. | Viscosity c.st. 98·9° C. | Index. | $d_4^{20}$. | $N_D^{20}$. | Spec. Refr. |
|---|---|---|---|---|---|---|---|
| *N* | 0·05 | 160·0 | 9·9 | −1 | 0·9249 | 1·5093 | 0·3230 |
| *Q* | 0·65 | 114·9 | 11·8 | 99 | 0·8819 | 1·4904 | 0·3281 |
| *W* | 0·83 | 137·0 | 13·6 | 102 | 0·8795 | 1·4890 | 0·3282 |
| *V* | 0·70 | 111·7 | 12·1 | 106 | 0·8750 | 1·4864 | 0·3284 |
| *M* | 0·47 | 145·0 | 12·1 | 76 | 0·8997 | 1·4997 | 0·3267 |

| Oil. | Anil. Point. | Mol. Weight. | Spec. Disp. | % Aromatics. | % Naphthenes. | % Paraff. Side Chains. |
|---|---|---|---|---|---|---|
| *N* | 86·2 | 397 | 190 | 12 | 36 | 52 |
| *Q* | 113·0 | 530 | 181 | 7 | 15 | 78 |
| *W* | 117·2 | 555 | 170 | 5 | 14 | 81 |
| *V* | 119·2 | 552 | 168 | 4 | 13 | 83 |
| *M* | 103·0 | 490 | 187 | 10 | 20 | 70 |

The "ring composition" was calculated from the constants *without* hydrogenation, as described by Vlugter, Waterman and van Westen (*J.I.P.T.* (1935), **21**, 671).

The oils *Q*, *W* and *V* were paraffinic base oils, oil *N* was a naphthenic base—and oil *M* a mixed base oil. Further, an oil *C* and an oil *E* were investigated. Oil *C* was a compounded oil containing (according to the

TABLE II.

| Oil. | Coefficient of Static Friction. |
|---|---|
| *Q* | 0·181 |
| *N* | 0·173 |
| Med. Paraff. Oil | 0·172 |
| *M* | 0·163 |
| *W* | 0·152 |
| *V* | 0·151 |
| *C* | 0·149 |
| *E* | 0·135 |

saponification-number) about 6 per cent. rape-oil and oil *E* a volt-oil prepared according to the well-known processes of de Hemptinne. In judging the results obtained for the volt-oil, it should be remembered that in this process certain quantities of fatty oils are generally added to introduce the reaction.

The results obtained for the coefficient of static friction are collected in Table II.

From this table it appears that it is not the base of the oil which is responsible for the coefficient of static friction, since, of the paraffinic-base oils examined, one has the highest coefficient obtained for mineral oils, the other the lowest. This is in accordance with the theory of polar compounds, which claims that certain compounds independent of the base of the oil are responsible for the value of the coefficient of static friction.*

However, it is possible that naphthenic-base oils are more liable to form acids, which act as polar compounds, and consequently lower the coefficient of static friction, than paraffinic-base oils. That compounds are formed on storage which lower the coefficient of static friction is proved by the fact that oil *Q*, which had originally a coefficient 0·181, after five months' storage attained a value 0·150. Further, oil *N*, which had an original value 0·173, attained, after the same period, an end-value 0·155, while oil *V*, which had an original low value 0·151, attained, after the same period, an end-value 0·150 and was also unchanged. It is well known that fatty acids should be regarded as polar compounds; the low value found for the coefficient of static friction of oil *C* is fully in accordance with this.

The low value found for the volt-oil *E* is very interesting. It is not clear whether the fatty oil added, or a modification of the molecule as a result of the electrical treatment, is responsible for this. The medicinal paraffin oil behaved during the test entirely differently from the other oils, viz. the equilibrium was reached immediately, indicating that no polar compounds were present; the subsequent values 9·8, 9·6, 9·5, 9·9, 9·7, 9·6, 9·8, 9·9, 9·9, 9·7, 9·7 during the first day, and 9·9, 9·6, 9·7, 9·8, 9·7, 9·7, 9·9, 9·7, 9·7, 9·5, 9·7 and 9·5 during the second day were noticed.

TABLE III.

| Oil. | Oil as such. | 0·5% AA-compound added. |
|---|---|---|
| *Q* . . . . . | 0·181 | 0·138 |
| *V* . . . . . | 0·151 | 0·138 |
| *E* . . . . . | 0·135 | 0·141 |

In the literature, static-friction reducers are often described. These are mostly fatty acids or other compounds which contain polar groups. For the influence of fatty acids we refer to the paper of Redgrove, who describes very thoroughly the results which can be obtained by adding these compounds, and who finds that the reduction in friction produced by the fatty

* See Lubrication Research. Technical Paper No. 1. "The Analysis of Commercial Lubricating Oils by Physical Methods." H.M. Stationery Office, London 1936.

acids is proportional to the length of the hydrocarbon chain, normal to the bearing surfaces, attached to the absorbed polar group.

In this investigation we tested neutralized fatty acids, recommended under the trade name AA-compound.

To the oils *Q*, *V* and *E*, ½ per cent. of this compound was added, with the result given in Table III.

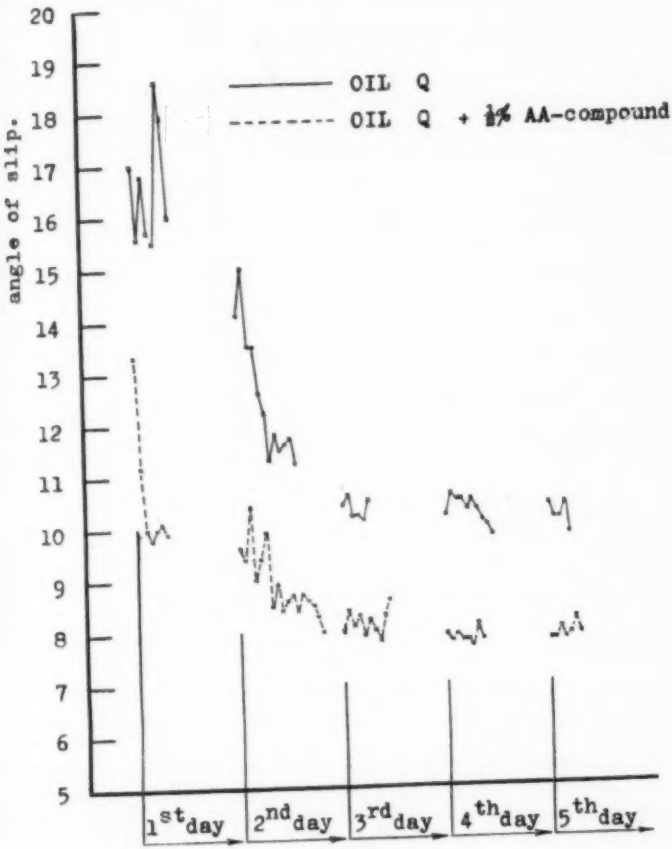


FIG. 3.

We see from this that the expected lowering in coefficient of friction of oils with a high coefficient really exists. The compounded oil, however, tends to a certain limiting value. If the coefficient is below this value, then the addition of the compound eventually causes an increase in the coefficient. In Fig. 3 the whole curves measured for oil *Q* as such and after adding 0·5 per cent. AA-compound are given.

From this it appears that the curve for the compounded oil is not only much

lower than that of the original oil, but that there is also a tendency to reach the end-value more rapidly.

In view of the considerable fall in coefficient of friction by the addition of only small quantities of polar compounds, it is reasonable to ask what will be the effect of the addition of an oil with a low coefficient on an oil with a high coefficient.

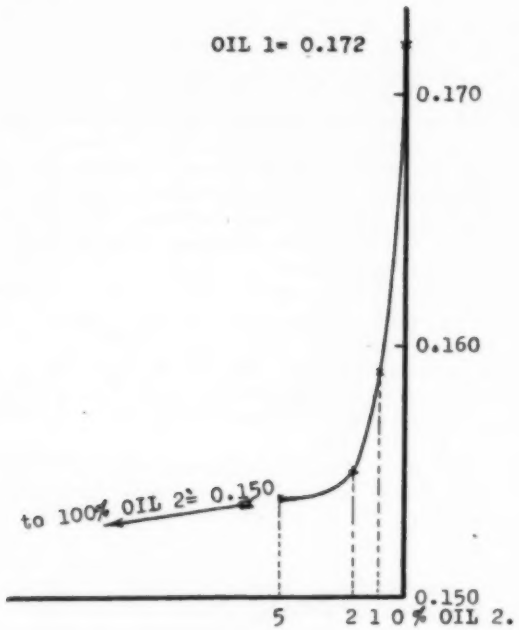


FIG. 4.

To test this we mixed medicinal paraffin oil with a coefficient 0·172 with different quantities of a mineral oil with a coefficient 0·150 (oil *V* after a 5 months' period of storage).

In Fig. 4 the results are graphically represented. It is apparent that not only the addition of concentrated polar compounds, but the addition of relatively small quantities of an oil with a low coefficient of static friction will also have a very important effect.

# HYDROGENATION OF SOME BENZENE HYDROCARBONS UNDER HIGH PRESSURE.

By M. K. Diakova, A. V. Losovoy and T. G. Stepantzeva.

A series of investigations has been carried out on the hydrogenation of monocyclic hydrocarbons under various conditions of pressure and temperature and with different apparatus and catalysts.

The principal investigations in this field belong to P. Sabatier and Senderens, R. Willstätter, N. D. Zelinsky and their co-workers.

However, some benzene homologues—for instance, pentamethylbenzene—have not yet been subjected to hydrogenation. Some other hydrocarbons of this series, such as hexamethylbenzene, have been hydrogenated under conditions that do not exclude the possibility of side reactions. A number of simpler benzene hydrocarbons, propylbenzene, *o*-, *m*- and *p*-xylenes and durene have not yet been hydrogenated under high pressure of hydrogen, one of the most convenient laboratory procedures for preparing six-membered naphthenes. Besides this, many discrepancies are observed in literature concerning the properties of hexahydrodurene. The above-mentioned considerations and the necessity to synthesize a number of six-membered naphthenes have led us to undertake this investigation.

## Hydrogenation of Hexamethylbenzene.

The hydrogenation of the completely alkylated benzenes has a peculiar interest because compounds of this type are in many ways different from all other benzene homologues. These hydrocarbons have perfectly symmetric molecules, approaching in symmetry the benzene molecules, and the symmetrical structure accounts for the lack of activity in these compounds. While benzene or its partly substituted homologues in their aromatic nucleus contain atoms of hydrogen, which determine the reaction capacity of these compounds, the completely substituted benzene has no such atoms, a circumstance that produces additional stability of these molecules. It is, moreover, highly probable that unsaturated linkages of a benzene nucleus containing unsubstituted hydrogen atoms differ in character from unsaturated linkages in a completely alkylated nucleus. Further, radicals surrounding the aromatic nucleus may cause some steric difficulty to the addition of hydrogen. Therefore we see that there is reason to anticipate considerable difficulties in the way of hydrogenating hexa-alkylbenzenes, and one may even doubt the possibility of producing such a reaction. The stability of hexamethylbenzene towards the addition of hydrogen ought to be particularly great, and may even exceed the well-known stability of benzene itself.

The first experiments of hydrogenation of hexamethylbenzene were made a short time ago by A. Dros, A. I. Tulleners and H. I. Waterman,[1] who used a nickel catalyst, and obtained liquid products of

hydrogenation. They isolated from this liquid several fractions with a boiling temperature of 195–203°, specific gravity $d_4^{20} = 0{\cdot}8185 - 0{\cdot}8265$, refractive index $n_D^{20} = 1{\cdot}4490 - 1{\cdot}4531$ and aniline point 65–66°, which correspond to hexamethyl*cyclo*hexane. The authors regard these fractions as a mixture of isomeric hexamethyl*cyclo*hexanes; it is, however, not evident what kind of isomerism they imply: *cis-trans*-isomerism, or substitution isomerism, or both. The operating conditions employed by Dros, Tulleners and Waterman (especially the very high temperature 300–310°) make the supposition of side-reactions probable.

Our experiments have shown that it is exceedingly difficult to effect the hydrogenation of hexamethylbenzene. Among the twelve monocyclic hydrocarbons with which we have been dealing, including benzene and its monoalkyl derivatives with side-chains of different length and polymethyl derivatives, the rate of hydrogenation is the lowest for hexamethylbenzene. Its rate is about 60 times less than that of toluene. We have succeeded in effecting a complete hydrogenation of hexamethylbenzene at 200–220° and a pressure of hydrogen 200–230 atm. using nickel oxide as a catalyst. In this case the yield of 1 : 2 : 3 : 4 : 5 : 6-hexamethyl*cyclo*hexane boiling at 210–216° and with $n_D^{20} = 1{\cdot}4606$ (fraction 210–214°) and 1·4638 (fraction 214–216°), $d_D^{20} = 0{\cdot}8405$ (fraction 210–214°) and 0·8461 (fraction 214–216°) and aniline point 56·2–56·9° was 60 per cent. *Both the above-mentioned fractions, according to their elementary composition, molecular weight and molecular refraction, correspond to the formula* $C_{12}H_{24}$ *and the method of its synthesis determines the structure for this naphthene as* 1 : 2 : 3 : 4 : 5 : 6-*hexamethyl*cyclo*hexane*. Our sample is probably a mixture of *cis-* and *trans*-isomerides. We have observed no splitting-off of methyl groups, but we have obtained a considerable yield (about 30 per cent.) of a fraction with a wide boiling range (190–210°) and with an aniline point 57–58°. We have not, however, been able to subject this product to a more detailed investigation, owing to its small quantity.

Hydrocarbons of the composition $C_{12}H_{24}$ and boiling range 211–216° isolated by Mabery from various petroleums differ in their properties from our sample.

### Hydrogenation of Pentamethylbenzene.

Pentamethylbenzene has not yet been subjected to hydrogenation, and the corresponding naphthenic hydrocarbon 1 : 2 : 3 : 4 : 5-pentamethyl*cyclo*hexane was hitherto unknown. The structure of pentamethyl*cyclo*hexane obtained by R. Stratford,[2] together with other hydrocarbons as products of cracking *iso*amyl*cyclo*hexane in presence of aluminium chloride, has not been ascertained, and considering the conditions of this reaction, one can admit that various isomers of the formula $C_{11}H_{22}$ are present.

Differing from hexamethylbenzene, pentamethylbenzene is rather easy to hydrogenate, and at 210–230° in the presence of a nickel catalyst and under a pressure of hydrogen 130–140 atm. it is converted into a mobile colourless liquid with a pleasant odour, boiling temperature 183–187° (752 mm.) $d_4^{20} = 0{\cdot}8200$ (fraction 183–186°) and 0·8214 (fraction 186–187°), $n_D^{20} = 1{\cdot}44995$ (fraction 183–186°) and 1·45035 (fraction 186–187°) and an aniline point 57·75°.

By its elementary composition, molecular weight and molecular refraction this substance corresponds to the formula $C_{11}H_{22}$, and according to the method of its synthesis, it must have the structure of 1 : 2 : 3 : 4 : 5-pentamethyl*cyclo*hexane. Our hydrocarbon has a higher specific gravity and a higher refractive index than Stratford's pentamethyl*cyclo*hexane.

### Hydrogenation of 1 : 2 : 4 : 5-Tetramethylbenzene (Durene).

The hydrogenation of durene to 1 : 2 : 4 : 5-tetramethyl*cyclo*hexane has been carried out by R. Willstätter and D. Hatt,[3] who used a suspension of the hydrocarbon in glacial acetic acid with platinum-black as a catalyst under atmospheric pressure and at room temperature. We have hydrogenated durene with a nickel catalyst at 230–240° and a pressure of hydrogen 170 atm. The rate of reaction was much lower than in the case of other benzene hydrocarbons (except hexamethylbenzene). We observed no splitting-off of methyl groups. The yield of 1 : 2 : 4 : 5-tetramethyl*cyclo*hexane reached 65 per cent. (there was a considerable loss of hydrocarbon during the refining with 100 per cent. sulphuric acid). As to its properties, our sample corresponds to 1 : 2 : 4 : 5-tetramethyl*cyclo*hexane described by v. Auwers,[4] who produced it from 1-chlor-1 : 2 : 4 : 5-methyl*cyclo*hexane by reduction with sodium in moist ether, but our hydrocarbon is rather different from the hydrocarbon of Willstätter and Hatt (a much lower boiling point, lower specific gravity and refractive index). Willstätter and Hatt do not mention if they have made certain that their sample was free from traces of aromatic hydrocarbon. Such an impurity could increase $n$ and $d$. We found for our 1 : 2 : 4 : 5-tetramethyl*cyclo*hexane an aniline point 58·8°.

### Hydrogenation of the Three Xylenes and of Propylbenzene.

All these compounds have been converted into corresponding naphthenes by Sabatier and Senderens and their co-workers by means of hydrogenation under atmospheric pressure.

We have found that by using the method of hydrogenation under high pressure *o*-, *m*- and *p*-xylenes and *n*-propylbenzene can be easily converted into six-membered naphthenes. This process has been carried out in an immobile autoclave at 220–240°, operative pressure 120–130 atm., and in the presence of reduced nickel as a catalyst. There occurs no splitting-off of side chains. Naphthenic hydrocarbons are obtained with a good yield, and the process can be carried out almost to the end (95 per cent.). The properties of our naphthenes were similar to those described in literature by other authors.

### Experimental.

Electrolytic hydrogen has been used in all our experiments. For the determination of aniline points we have used a freshly distilled aniline with m. p.—6·2° obtained from its sulphate.

#### (a) *Hydrogenation of Hexamethylbenzene.*

We have prepared hexamethylbenzene by methylation of xylene with methyl chloride in the presence of aluminium chloride according to Friedel

and Krafts, under conditions given in the book "Organic Synthesis" (1922) Vol. II. After numerous recrystallizations from ethyl alcohol we obtained hexamethylbenzene with melting point 159–160°.

We have also studied the behaviour of this hydrocarbon towards sulphuric acid, because the data given by different authors do not accord.[5]

For this purpose we prepared a 7 per cent. solution of hexamethylbenzene in methyl*cyclo*hexane. $n_D^{20}$ of methyl*cyclo*hexane was 1·4231, $n_D^{20}$ of the solution = 1·4326, after the treatment with 3 volumes of 99 per cent. sulphuric acid the solution had $n_D^{20} = 1·4233$, which means that sulphuric acid totally removes hexamethylbenzene from its solution.

25 gm. of hexamethylbenzene were placed in a 0·5-l. rotating autoclave together with 2·5 gm. of nickel oxide prepared from nickel nitrate by heating it in the air at a temperature below 450°. The initial pressure of hydrogen was 135 atm., the operative pressure 200–230 atm. and the temperature of hydrogenation was maintained at 200–220°. Twenty hours were needed for the completion of the reaction. The products discharged after 10 hours' heating contained a considerable amount of hexamethylbenzene. The gases of hydrogenation contained no methane. We obtained 24 gm. (29 c.c.) of a mobile and colourless liquid with a pleasant terpeneous odour. This liquid had a refractive index $n_D^{20} = 1·4627$ and a boiling range 200–220°, the main quantity boiled between 214 and 218° leaving no crystalline residue. This liquid product was treated with 3½ volumes of 99 per cent. sulphuric acid, and no change of volume was observed. It had a refractive index $n_D^{20} = 1·4622$. After shaking with two volumes of 100 per cent. sulphuric acid it had $n_D^{20} = 1·4620$.

After washing and drying the product was fractionated and divided into three fractions (Table I).

TABLE I.

| Fraction. | Gm. | B. p. at 760 mm. | $n_D^{20}$. | $d_D^{20}$. | $MR_D$. | Mol. weight. | Aniline point. | % C. | % H. |
|---|---|---|---|---|---|---|---|---|---|
| I | 4 | 206–210° | 1·4580 | 0·8349 | 55·10 | 158; 157 | 58·2 | 85·05 | 14·76 |
| II | 7·8 | 210–214° | 1·4606 | 0·8405 | 54·94 | 169; 170·7 | 56·9 | 85·35 | 14·50 |
| | | | | | | | | 85·62 | 14·66 |
| III | 6·35 | 214–216° | 1·4638 | 0·8451 | 54·80 | 169; 170 | 56·2 | 85·65 | 14·58 |
| | | | | | | | | 85·55 | 14·20 |

Calculated elementary composition $C_{12}H_{24}$: C = 85·62 per cent.; H = 14·38 per cent.
" molecular weight " 168
" " refraction (D) " 55·4

(b) *Hydrogenation of Pentamethylbenzene.*

Pentamethylbenzene was obtained, together with durene and hexamethylbenzene, by means of the above-mentioned method of methylation of the xylenes with methyl chloride in the presence of aluminium chloride. After numerous recrystallizations from alcohol we obtained a pure sample of pentamethylbenzene as white plates with a melting point 51–52°, specific gravity $d_4^{45} = 0·8895$, refractive index $n_D^{60} = 1·50933$ and molecular refraction $MR_D = 49·68$. Calculated $MR_D$ for $C_{11}H_{16}$ with three double bonds 49·40.

25 gm. of pentamethylbenzene and a nickel catalyst freshly reduced from 10 gm. of nickel carbonate at 320–340° were placed in a 0·5-l. rotating autoclave. Initial pressure of hydrogen was 80 atm., the temperature 210–230°, the duration of the process 6 hours. The gases of hydrogenation contained no methane. We obtained 26 c.c. of a mobile, colourless, transparent liquid with a terpeneous odour. It had the following constants: $d_4^{20} = 0{\cdot}8251$, $n_D^{19{\cdot}5} = 1{\cdot}4535$ and boiling range 173–198·50 per cent. at 184–188°. After distilling 0·8 gm. of crystalline residue remained in the flask.

The whole fraction 173–198° was treated once with 99 per cent. sulphuric acid (3½ volumes) and twice with 2 volumes of oleum (83 per cent. $SO_3$); the refraction after treatment with oleum gave no change. The shaking with 99 per cent. acid gave no change of volume, but the last treatment with oleum caused a considerable loss of hydrocarbons, probably of naphthenes. We obtained 8·5 gm. of a fraction with a boiling temperature 183–186°/(752 mm.) refractive index $n_D^{20} = 1{\cdot}44995$ and specific gravity $d_4^{20} = 0{\cdot}8200$, and 3·2 gm. of a fraction with boiling temperature 186–187°, $n_D^{20} = 1{\cdot}45035$ and $d_4^{20} = 0{\cdot}8214$. These fractions are therefore near to one another in composition.

The fraction 183–186° has a molecular weight (benzene freezing-point method) 152 (calculated 154), an elementary composition (a mean value from two analyses) C = 85·95 per cent. and H = 13·95 per cent. (1) 0·1620 gm. subst.; 0·5108 gm. $CO_2$; 0·2034 gm. $H_2O$; found per cent.: C = 85·99, H = 14·03. (2) 0·1775 gm. subst.; 0·5584 gm. $CO_2$, 0·2198 gm. $H_2O$; found per cent.: C = 85·90, H = 13·84. Calc. for $C_{11}H_{22}$: C = 85·71; H = 14·29; $MR_D = 50{\cdot}35$ (Calc. $MR_D$ 50·80). Aniline point 57·75°, $d_4^{20} = 0{\cdot}7990$; $n_D^{20{\cdot}2} = 1{\cdot}43840$.

Stratford's data (*loc. cit.*) for pentamethyl*cyclo*hexane of an undetermined structure (formula $C_{11}H_{22}$ is only proved) are: b. p. 180–185°; $d_4^{11} = 0{\cdot}8081$; $n_D^{11} = 1{\cdot}44550$.

A naphthenic hydrocarbon $C_{11}H_{22}$ isolated from petroleum had b. p. 180° and $d = 0{\cdot}8119$.[6]

### (c) *Hydrogenation of Durene.*

Durene was synthesized according to the method described in the book "Organic Synthesis" Vol. II (1922). After numerous recrystallizations from alcohol we obtained a perfectly white crystalline substance that had a sharp melting point 79° and a refractive index $n_D^{86} = 1{\cdot}48330$. The literature data are: m. p. 79° and 80°, $n_D^{81{\cdot}3} = 1{\cdot}47896$, $d_D^{81{\cdot}3} = 0{\cdot}8380$. 13 gm. of durene and 2 gm. of nickel oxide (see hexamethylbenzene) were placed in a 0·5-l. rotating autoclave. The initial pressure of hydrogen was 100 atm., the operative pressure 170 atm., the temperature 220–240°, the duration of heating 10 hours, the final pressure 88 atm. The gases of hydrogenation contained no methane. We obtained 12 gm. of a liquid product boiling at 160–170° with $n_D^{20} = 1{\cdot}43913$. This liquid was treated with 3½ volumes of 99 per cent. sulphuric acid wherever we observed no loss of hydrocarbon. A second treatment with two volumes of 100 per cent. sulphuric acid was followed by a noticeable loss of hydrocarbon. The treated product was washed, dried and distilled. We obtained the following fractions.

(1) 160–161·5°/(751 mm.) = 8·5 gm., $n_D^{20} = 1{\cdot}43717$, $n_D^{40} = 1{\cdot}4299$, $d_4^{20} = 0{\cdot}7934$, $d_4^{0} = 0{\cdot}7578$, aniline point 58·8°, molecular weight 139 and 139·5; $MR_D = 46{\cdot}24$.

(2) 161·5–162·5° = 1 gm.

The theoretical values for $C_{10}H_{20}$ are: molecular weight 140 and molecular refraction $MR_D = 46{\cdot}18$.

Literature references for 1 : 2 : 4 : 5-tetramethyl*cyclo*hexane are as follows: Willstätter and Hatt $K_{p711} = 169–170{\cdot}5$, $d_4^{0} = 0{\cdot}825$, $d_4^{19} = 0{\cdot}811$; $n_D^{20} = 1{\cdot}4451$. v. Auwers: $K_p = 160{\cdot}5–161{\cdot}5°$, $d_4^{13{\cdot}1} = 0{\cdot}7910$, $n_D^{13{\cdot}1} = 1{\cdot}4370$.

### (d) *Hydrogenation of* o-*Xylene.*

From a sample of Kahlbaum's "reinst" *o*-xylene there was isolated a fraction with $K_{p742} = 142{\cdot}4–142{\cdot}5°$, $d_4^{20} = 0{\cdot}8783$, and $n_D^{20} = 1{\cdot}50477$.

Twenty gm. of this *o*-xylene were placed in an immobile 0·6-l. autoclave and a nickel catalyst obtained by reduction of 10 gm. of nickel carbonate with hydrogen at 320–340° was added. The initial pressure was 100 atm., the temperature of reaction 220–240°, the period of heating 12 hours. After cooling, the pressure was 80 atm. There was obtained 18·7 gm. of a liquid with a boiling point 121–125° and $n_D^{20} = 1{\cdot}43086$. The treatment with 3 volumes of 99 per cent. sulphuric acid was not followed by any noticeable diminution of volume. By repeated fractionation there were isolated 16·5 gm. of a fraction corresponding to 1 : 2-dimethyl*cyclo*hexane with a b. p. (748 mm.) 122·5–124°, $d_4^{20} = 0{\cdot}7814$, $n_D^{20} = 1{\cdot}42930$ and aniline point 44·9°, 44·85°.

### (e) *Hydrogenation of* m-*Xylene.*

We have prepared *m*-xylene according to the method of Konovaloff[7] (taking into consideration the indications given in the papers of A. Reuter[8] and E. Nölting and E. Forel.[9]) 1 part of common xylene was heated with 3 parts of nitric acid ($d = 1{\cdot}115$) on a steam bath with a reflux cooler during 10 hours.

Under these conditions *o*- and *p*-xylenes are oxidized, but *m*-xylene remains almost without any alteration. After proper refining and distilling we have isolated a fraction of *m*-xylene with a b. p. (740 mm.) 138–138·3°, $d_4^{20} = 0{\cdot}8641$ and $n_D^{20} = 1{\cdot}49741$. 30 gm. of *m*-xylene have been subjected to hydrogenation during 20 hours under almost the same conditions as those given for *o*-xylene. The final pressure was 72 atm. We obtained 29 gm. of a liquid product of hydrogenation with $n_D^{20} = 1{\cdot}42812$ and boiling range 119–123°. The liquid was treated with 3½ vol. of 99 per cent. sulphuric acid; no increase of the acid layer was observed. Thereupon we subjected the sample to a treatment with 2 volumes of oleum (83·0 per cent. $SO_3$), and then about 7 per cent. of hydrocarbon was removed. After washing, drying and distilling over sodium we collected 25·5 gm. of a fraction with a boiling point 119·5–120·5°/(740 mm.), $d_4^{20} = 0{\cdot}7677$, $n_D^{20} = 1{\cdot}42407$ and aniline point 49·5°.

### (f) *Hydrogenation of* p-*Xylene.*

From a sample of "reinst" Kahlbaum's *p*-xylene we isolated a fraction with a b. p. 137·3–137·5°/(740 mm.), $d_4^{20} = 0{\cdot}8609$, $n_D^{20} = 1{\cdot}49552$. 20 gm. of this fraction were subjected to hydrogenation during 17 hours under

conditions given above for *ortho*-xylene. After cooling, the pressure in the bomb was 80 atm. We obtained 18·5 gm. of a hydrogenated product with $n_D^{19} = 1{\cdot}4285$, b. p. 118–121°. This product was treated twice with 2 volumes of oleum (83 per cent. $SO_3$), and there occurred a noticeable diminution of the volume of hydrocarbon. After washing with alkali and water, drying and distilling we isolated 16·2 gm. of the main fraction with b. p. 119·5–120°/(740 mm.), $d_4^{20} = 0{\cdot}7669$, $n_D^{20} = 1{\cdot}42326$ and aniline point 49·45°.

(g) *Hydrogenation of* n-*Propylbenzene.*

*n*-Propylbenzene was produced according to Fittig's reaction by the action of sodium on a mixture of 1-brompropane and brombenzene. From the reaction products we isolated a fraction that by its boiling point corresponded to *n*-propylbenzene. After boiling this fraction under reflux with metallic sodium and after many distillations over sodium we obtained *n*-propylbenzene with the following constants: $K_{p735} = 155{\cdot}4$–$156{\cdot}4°$, $n_D^{20} = 1{\cdot}49192$, $d_4^{20} = 0{\cdot}8618$.

21 gm. of *n*-propylbenzene were placed in the bomb, and the hydrogenation was carried out under conditions given for *o*-xylene. The hydrogenation lasted 22 hours, the final pressure was 83 atm. We obtained 19·9 gm. of a liquid product boiling at 151–156° with $n_D^{20} = 1{\cdot}4378$. After treatment with 3½ volumes of 99 per cent. sulphuric acid we noticed no change of volume, the product had a boiling point 153–155°, $d_4^{20} = 0{\cdot}7926$, $n_D^{20} = 1{\cdot}43678$. A further treatment with 2 volumes of oleum (containing 83 per cent. $SO_3$) was followed by a considerable loss (15 per cent.) of hydrocarbon, and we obtained 15·3 gm. of *n*-propyl*cyclo*hexane boiling at 154–155°/(745 mm.), $d_4^{20} = 0{\cdot}7930$, $n_D^{20} = 1{\cdot}43690$, aniline point 50·5°, $MR_D = 41{\cdot}58$, $MR_D$ calc. for $C_9H_{18} = 41{\cdot}56$.

## Conclusions.

1. It has been shown that hexamethylbenzene, pentamethylbenzene, 1 : 2 : 4 : 5-tetramethylbenzene, *o*-, *m*-, *p*-xylenes and *n*-propylbenzene can be transformed into corresponding six-membered naphthenes by means of hydrogenation with a nickel catalyst, under pressure of hydrogen from 120 to 230 atm. and at a temperature of 200–240°. The reaction is not followed by any splitting-off of the side chains.

2. New naphthenes: 1 : 2 : 3 : 4 : 5 : 6-hexamethyl*cyclo*hexane and 1 : 2 : 3 : 4 : 5-pentamethyl*cyclo*hexane have been obtained and described.

New constants for some naphthenes have been determined.

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## *CORRESPONDENCE.*

*To the Editor.*

SIR,

*Anomalous Results for Soluble Bitumen of Natural Rock Asphalts.*

In a recent communication, A. A. Ashworth (*J.I.P.T.*, 1937, **23** (162), 266) has described some anomalous results obtained for the soluble bitumen content of a naturally impregnated limestone. Extraction in the cold with carbon disulphide gave 5 per cent. soluble bitumen, whereas hot extraction with trichlorethylene gave 9·5 per cent. Further, the bitumen extracted by carbon disulphide was much softer in consistency than that obtained using trichlorethylene. The tentative explanation advanced was that the mineral matter associated with the rock strongly adsorbed the hydrocarbons of higher molecular weight and prevented their extraction by carbon disulphide, although not by hot trichlorethylene.

As no details regarding the constitution of the mineral matter or source of origin of the natural rock are given, it is difficult to assess the merits of the theory or to ascertain the possibility of such a rock appearing on the market in this country. The results nevertheless raise the important question as to what constitutes the soluble bitumen content of a bituminous rock. The International and British Standard definitions of bitumen include in this term only those hydrocarbons and their non-metallic derivatives which are completely soluble in carbon disulphide. Recently, the use of such solvents as trichlorethylene has been permitted by the British Standards Institution for the determination of soluble bitumen (B.S.S. 598), on the tacit assumption that the results will be identical with those obtained when using carbon disulphide, but this does not alter the fact that the latter is the standard international solvent. If it should be found, therefore, that a rock asphalt is impregnated with a mixture of hydrocarbons partly soluble in carbon disulphide but wholly soluble in hot trichlorethylene, only the former could legitimately be construed as bitumen. The position is naturally altered if the bitumen is actually soluble in carbon disulphide, but is adsorbed in such a manner that it cannot be extracted with the cold solvent under normal conditions. In this case it would certainly appear that some modification of the standard method is desirable.

Results obtained some time ago in Geochemical Laboratories on a sample of Egyptian rock asphalt may possibly have some bearing on the reason for the discrepancy noted by A. A. Ashworth. The rock was a very hard, compact, uniform, fine-grained asphaltic limestone. A soluble bitumen determination carried out on the finely crushed rock by extraction with cold carbon disulphide gave a figure of 4·4 per cent. soluble bitumen. The fact that a portion of the residue after grinding in an agate mortar and re-extracting with carbon disulphide gave no appreciable amount of bitumen indicated that the extraction had been carried almost to completion. The appearance of the residue, and its behaviour on ignition, nevertheless, indicated that a considerable amount of bituminous material was still present. An excess of ether–hydrochloric acid (prepared by saturating

concentrated hydrochloric acid with ether and cooling with water) was added to the residue from the first carbon disulphide extraction and the mixture stirred until effervescence ceased. Hot water was then added, and the beaker allowed to stand until the ether had evaporated, when the solution and insoluble matter were poured through a filter and the insoluble matter was washed free from mineral acid. The insoluble matter was dried and extracted with cold carbon disulphide, and the bitumen solution poured through a filter paper and collected in a weighed dish. This solution after evaporation to dryness gave 2·0 per cent. of bitumen, normal in appearance, but having an acid value of 137 mgms. KOH/gm. It is probable therefore that it was present in the original rock asphalt as a soap. The residue insoluble in carbon disulphide on extraction with cold trichlorethylene yielded a further quantity of " bitumen " amounting to 1·9 per cent. of the original rock. This also was normal in appearance, but had a very high acid value (149 mgms. KOH/gm.). Finally, the residue, from the trichlorethylene extraction was extracted with pyridine, and 8·9 per cent. of organic matter (probably pyrobitumens) removed. The mineral residue was now comparatively free from organic matter and did not blacken on heating.

The total organic matter in this particular rock asphalt amounted to 17·2 per cent., and of this only 4·4 per cent. could be considered as soluble bitumen. The summary of the analysis is shown below :—

| | Per cent. |
|---|---|
| Bitumen soluble in cold $CS_2$ (normal extraction) | 4·4 |
| Bitumen (2nd $CS_2$ extraction after ether–HCl treatment) | 2·0 |
| Organic matter (trichlorethylene extraction) | 1·9 |
| Organic matter (pyridine extraction) | 8·9 |
| Calcium carbonate | 73·0 |
| Silica | 7·6 |
| Difference | 2·2 |
| | 100·0 |

It is difficult to explain why 1·9 per cent. organic matter was removed with trichlorethylene after the second carbon disulphide extraction, unless it was actually insoluble in the latter solvent. At this stage of the analysis, most of the mineral matter had been removed by the acid treatment and the possibility of adsorption is remote.

The presence of organic matter of this nature in conjunction with soap-like derivatives would be expected to lead to differences between the cold carbon disulphide and hot trichlorethylene extracts, particularly so if the extraction in the latter case was carried out under conditions favouring the hydrolysis of the solvent. In such circumstances trichlorethylene would not be a suitable substitute for carbon disulphide.

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# THE PRESENT STATE OF OUR KNOWLEDGE ON THE ORIGIN OF PETROLEUM.*

By C. D. Nenitzescu.

There are few scientific problems which have led to such a vast number of theories as that of the origin of petroleum. The difficulties arise from the fact that petroleum, unlike other natural fuels, has not preserved any apparent signs of the processes which have led to its formation, or of the raw material from which it originated.

Furthermore, the problem of the origin of petroleum is complicated by the various methods used in solving it. The effect of extreme specialization is felt here much more than in any other branch of science. Thus, chemists have tried to explain the origin of petroleum by purely laboratory experiments, geologists by observations of strata, whilst biologists have attempted to make use of recently observed phenomena. It is, however, evident that only by the close collaboration of several sciences, such as physical and organic chemistry, biological chemistry, bacteriology, limnology, oceanography and palæontology, can a positive result be achieved.

Men of science belonging to a certain branch of research have often worked without having any contact with the allied sciences, and this explains why so many perfectly plausible theories are contradicted by the results obtained by other methods of research. Thus, nearly all the great specialists in hydrocarbon chemistry during the last 70 years have considered it a point of honour to formulate a theory on the origin of petroleum.

All these theories discuss or propose the possibility of formation in the earth's crust of hydrocarbons more or less similar to natural petroleum. It is not, of course, of primary importance to discuss the possible ways of formation of these hydrocarbons. The problem consists in reconstituting the process of the historic succession of phenomena which have actually happened in nature.

It is apparent, therefore, that the vast literature on this subject has to be looked upon with a very critical eye, and in the following pages will be considered only those studies, the results of which are based, as far as possible, on facts and observations which are not contradicted by the results of other sciences.

## Classical Theories.

Among the theories which should have been discarded long ago but which, nevertheless, reappear periodically, are the so-called "inorganic" theories. They are based on the work of the great Russian chemist Mendeleeff, who succeeded in obtaining gaseous and liquid hydrocarbons by treating cast iron rich in carbon with hydrochloric acid. Iron ore with a considerable iron content occurs in large amounts in the incandescent parts of the earth's crust, and the fact that hydrochloric acid does not occur, and probably never has occurred in the free state in nature, does not seem to have hindered the dissemination of this theory. It was

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thought then that sea water, owing to its content of hydrolyzable magnesium chloride, might produce the same effect as hydrochloric acid when coming in contact with the incandescent layers of the earth, in spite of the little probability of such a phenomenon ever taking place. On the other hand, many meteorites were found to contain iron as well as carbon, hydrocarbons were detected in the tails of comets and in the atmosphere of some planets such as Jupiter, and all these facts were curiously looked upon as arguments in favour of the Mendeleeff theory.

Another group of "inorganic" theories are based on the catalytic hydrogenating reactions discovered by Sabatier and his collaborators, which, as is well known, have acquired great scientific and industrial importance. Even Sabatier himself, on observing that during the catalytic hydrogenation of acetylene, liquid hydrocarbons are obtained under certain conditions, has formulated such a theory for the origin of natural petroleum. The acetylene necessary for this reaction could only have been obtained by the action of water on metallic carbides which have never been found as such in nature.

The well-known Franz Fischer process for the synthesis of benzine from hydrogen and carbon monoxide has also been used for the postulation of a theory. The two gaseous raw materials were sometimes found even together in the volcanic gases, *i.e.* at Mont Pélé. The absence in nature of very sensitive catalysts required for this process, which are exceedingly influenced by traces of sulphur, does not appear to have produced any serious arguments against the spreading of this theory.

Very important arguments against these inorganic theories were formulated long ago by Engler and Höfer. They may be summarized as follows: petroleum never occurs in primary or igneous rocks, but always in sedimentary rocks, mostly of recent or tertiary formation: hydrogen has never been found in oilfield gases, as it should occur according to the carbide and hydrogenation theories, and finally, certain components are found in petroleum which are optically active, as well as nitrogen compounds, the origin of which it is absolutely impossible to explain according to the inorganic theories under the conditions prevailing in oil deposits.

Even in the case of the "organic" theories, we often find incompatibilities with regard to the other sciences, and especially geology.

Organic theories when put forward by chemists usually attempt to demonstrate that, starting from any kind of organic material, of animal or plant origin, by treatment with certain chemical or physical agents, a mixture more or less resembling natural oil may be obtained. A large number of such theories have been advanced, the most important being, of course, the famous Engler theory. Starting from the idea that petroleum is derived from animal material, quite different from coal, which is of plant origin, and based on the geologic research of Höfer, who has shown that petroleum originated in the sea, this author has distilled, under pressure, fish oils at a temperature of 300–400° C. In this manner he obtained a complex mixture of hydrocarbons resembling in a way natural petroleum, but differing from it by the high content of unsaturated hydrocarbons. Later research on oil deposits has shown, however, that such temperatures have never been reached and that distillation inside these deposits is entirely excluded.

Numerous other laboratory investigations deal with the destructive influence of various catalysts on the materials which might be considered as the mother substances of petroleum. The best known in this direction is the research undertaken by Zelinsky,[1] who distils substances of lipoidic nature such as fatty acids, cholesterol, phytosterol, beeswax, etc., with the most powerful catalyst known in this domain, *i.e.* aluminium chloride, and obtains, according to the raw material used, products resembling more or less naphthenic or paraffinous oils. We think it would be superfluous to point out the enormous difference between the laboratory processes and natural phenomena, where such catalysts as aluminium chloride never occur.

Starting from the idea that not only lipoids could have served as the mother substance of petroleum, but also carbohydrates, especially cellulose —the principal component of plants—and, on the other hand, assuming that enormous quantities of vegetable matter should have existed in the extraordinary life conditions when petroleum was formed, Berl[2] has attempted to transform cellulose into bitumen and liquid hydrocarbons. For this purpose cellulose was at first pre-carbonized with sodium hydrate in Bergius bombs at 310–330° C. and at 200 atmospheres, whereby a highly polymerized unsaturated product was obtained. This was hydrogenated with hydrogen, iron and iodine at 100 atmospheres and 450° C., yielding a mixture of lower and higher paraffins, slightly resembling natural petroleum.

All these researches, as well as other studies which we refrain from mentioning, only prove that, under certain powerful conditions of hydrogenation or of activation of the hydrogen atoms bound to the organic molecule, the most varied organic materials have a tendency to lose their oxygen and yield hydrocarbons. The very energetic conditions of reaction and such powerful catalysts which could never have occurred in nature, induce us to believe that these experiments bear only a very slight analogy to the real natural phenomena which occurred in the formation of petroleum.

## Main Aspects of the Problem.

Much more useful than the above theories are the meticulous and apparently modest experiments which attempt to collect facts and observations from the domain of reality. The time is not yet ripe to make a synthesis of these observations. We are still in the initial period when the collection of material must be our main preoccupation. The synthesis will be achieved easily and spontaneously on the day when sufficient experimental material is collected.

The facts that contribute effectively to the outlining of this problem may be obtained in three different ways, namely :

(1) By the exact knowledge of the various kinds of oils and bituminous material found in nature and by attempting to separate their components, even those occurring in small amounts. Only by a thorough knowledge of the composition of the product and by understanding the chemistry of the various components will it be possible to reach valid conclusions with regard to the transformations incurred by the hypothetical mother substance.

(2) By studying petroleum deposits and bituminous strata in general, with the object of finding the source rock of petroleum. Once this source rock is known in detail, certain conclusions may be reached as to the raw materials and conditions of the formation of petroleum.

(3) By studying certain phenomena of fossilization which occur even to-day and which enable us to discover the eventual mother substance. The raw material could have undergone quantitative variations during the different geological eras, but only slight qualitative changes, because during the various geological epochs the animals or plants from which petroleum originated were composed, the same as to-day, of carbohydrates, fats and proteins. It is therefore of primary importance to know the behaviour of these substances during the process of fossilization.

We shall now analyse the progress achieved in these three different lines of research :

## The Composition of Petroleum in Relation to its Origin.

It would be impossible to summarize, even briefly, all the results obtained recently on the composition of petroleum. We must admit, however, that even the main components of petroleum—the hydrocarbons—are the least known, especially with regard to the individuals possessing a higher molecular weight. We know next to nothing about the chemical composition of naphthenes and *iso*paraffins with a b. pt. above 150° C. and of aromatics boiling above 200° C. We can have but a very vague idea as to the formation of the paraffins, *iso*paraffins and higher naphthenes. A very complicated problem is the origin of aromatic hydrocarbons.[3] From the study of the thermal behaviour of various organic substances it is known that the formation of aromatics takes place at above 700° C., a temperature which could never have been reached by petroleum. On the other hand, the small amount of aromatic compounds found in plants and animals cannot explain the origin of the relatively high aromatic percentage of petroleum. It is evident that these hydrocarbons were not performed in the mother substance of oil : they were formed from it by a process of which we know next to nothing except that it took place at a low temperature. Research on higher naphthenes, side chains, and especially on methyl groups, might give indications as to the formation of these naphthenes, *i.e.* whether they are derived from the polymerization of olefins.

In addition to hydrocarbons, petroleum contains, in a small or very small proportion, certain substances the study of which leads to very important conclusions in connection with its origin.

The oxygen-containing components, *i.e.* naphthenic acids and phenols, appear to have, as we shall see below, a secondary origin, being derived from hydrocarbons by oxidation. Nothing can be said regarding the origin of sulphur compounds since they have been very little studied.

On the other hand, the nitrogen compounds which were found in petroleum furnish a precise proof of the organic origin of petroleum, since all nitrogen compounds found in nature are of either animal or vegetable origin.

It has also been known for a long time that petroleum contains small

quantities of certain optically active substances, a point considered from the outset as a proof of the organic origin of petroleum, since only in the bodies of animals and plants are optically active compounds formed.

Very interesting from this point of view is the recent detection of œstrone in certain natural oils.[4] The occurrence of œstrus or heat in castrated animals is due to a specific action of certain hormones, the structure of which has been established recently. These hormones are widespread in the animal kingdom, and have even been found in plants in very small amounts. It is interesting how these hormones were kept unmodified for such a long interval of time.

The most interesting result of this kind is the detection of *porphyrins* in petroleum and in various natural bituminous materials by A. Treibs of Munich.[5] These porphyrins are combinations of a complex structure having four pyrrole nuclei in their molecule. They are formed from the colouring matter of animals (hæmochromogen) or from the green colouring matter of plants (chlorophyll) by the loss of the metallic complex (iron or magnesium). In petroleum, porphyrins occur in the form of complex compounds of iron and vanadium, the latter metal being found very often in small amounts in petroleum.

The following four porphyrins were identified and their spectra determined: Desoxophylerithroetioporphyrin, $C_{32}H_{36}N_4$ (Porphyrin I), Desoxophylerithrin, $C_{32}H_{35}N_4$·COOH (Porphyrin II), meso-etioporphyrin, $C_{32}H_{38}N_4$ (Porphyrin III) and mesoporphyrin, $C_{32}H_{36}N_4(COOH)_2$ (Porphyrin IV).

These porphyrins occur in all asphalts and in not too light natural oils which have not undergone filtrations and which still contain heavy asphaltic components. The amounts vary largely according to the origin of the oil. In a very interesting paper, Treibs has studied petroleum derived from nearly all parts of the world, and has found that in nearly half of the samples examined the porphyrin content amounts to 0·004–0·02 mg. in 100 grm., whilst in the remaining half the proportion rises from 0·4 to 4 mg. per cent. Trinidad asphalt contains 0·04 per cent. porphyrins, whilst that of Merida contains 0·4 per cent., an enormous amount if we consider that green leaves contain approximately 0·8 per cent. chlorophyll.

No porphyrins were found in petroleum of very old formation such as Pennsylvania and Virginia (Carboniferous and Devonian). In these very old oils, even if they once contained porphyrins, in the long run they decomposed, time having the same effect as high temperature. Porphyrins were found, however, in certain very old bituminous schists in Esthonia dating from the Carboniferous, Silurian and Devonian periods. This is explained by the exceptional way in which these schists have been preserved; thus they occur even to-day in horizontal strata in which they possibly originated, without suffering any high pressure or temperature.

The porphyrins I and II mentioned above are of a vegetable origin, being derived from chlorophyll, the other two, III and IV, being of animal origin. It has been found that vegetable porphyrins occur in much larger amounts than animal porphyrins, which is a very significant phenomenon, inasmuch as vegetable porphyrins are much less resistant chemically than animal porphyrins. Oils containing exclusively one of these porphyrins have not been found until to-day.

These results furnish the solution of an old problem, *i.e.* that of the

animal or vegetable origin of petroleum : the raw material from which petroleum originated must have been undoubtedly mostly of vegetable origin, and only in a smaller degree, or even accidentally, were materials of animal origin included in the primitive process of bituminization.

From the study of petroleum porphyrins very important conclusions were reached with regard to the maximum temperatures attained during the process of bituminization : porphyrin I was obtained from porphyrin II by the loss of one molecule of carbon dioxide under the action of heat and, likewise, porphyrin III from porphyrin IV. On the other hand, porphyrin II is formed from chlorophyll also by a thermal reaction. These reactions were studied also in the laboratory under conditions as far as possible similar to those prevailing in nature. It was found that the temperature at which chlorophyll dissolved in oil is transformed into porphyrin II and I is 250° C. Since time, if very long, may replace temperature, it may be admitted that the temperature of oil deposits containing porphyrins has never exceeded 200° C., this figure being an upper limit which has probably never been reached.[6] These findings show that petroleum could not have been subjected at any moment of its evolution to a higher temperature than that corresponding to the depth of the deposit. It has been established that in all the oilfields composed of sedimentary rocks the geothermic gradient is normal. If we admit that the lowest depth at which oil occurs does not exceed 5000 metres, the temperature could not have been over 160° C. and the pressure 1000 atmospheres.

Another consequence of the occurrence of porphyrins in petroleum relates to the nature of the medium in which bituminization took place. This medium had to be exceedingly reducing at the outset, because both chlorophyll and porphyrins are sensible to oxidation, and in the presence of an oxidizing medium they would have been quickly destroyed. On the other hand, both animal porphyrins are derived from mesoporphyrin, a compound differing from the colouring matter of blood (hæmochromogen) by the fact that it contains ethyl groups $-CH_2 - CH_3$ instead of vinyl groups $- CH = CH_2$. The formation of these groups may be explained only by a powerful hydrogenation which could have resulted from bacterial action or the action of heat due to the activation of the hydrogen atoms of the hydrocarbon molecules present.

## Petroleum Deposits.

Classical geology, by the study of various oil deposits, has been able to specify a series of characteristics common to all deposits. This study, in order to be useful, had to include not only productive oil deposits, but also various bituminous deposits, more or less abundant, which are very widely disseminated in nature.

Oil deposits occur far from volcanic regions, which excludes an inorganic or cosmic origin; they are far from coal seams, and even if occurring in their neighbourhood are not connected, having different conditions of formation.

Oil deposits occur often near mountains and salt massifs. In such regions the earth's crust has suffered a powerful folding, which has produced a considerable pressure upon the strata. These phenomena have given rise

probably to the internal seas or lagoons in which the beginning of bituminization took place, and which later on were evaporated. The present state of deposits has been undoubtedly determined by the production of faults and anticlinals.

These facts, known for a long time, constitute the basis of the Engler and Höfer classical theory.

Besides oil, we find in deposits salt water rich in sulphuretted hydrogen and with a high iodine content. Further, we find sulphides, especially of iron, which prove that the medium was rather reducing.

Attempts were made to explain the origin of this brine in oil deposits by the dissolution of salt massifs in the waters of infiltration. However, in addition to the fact pointed out by Mrazec,[7] that the existence of oil deposits is the most powerful proof that no infiltration of surface waters could have occurred in these deposits, which would have destroyed them, as happens to-day in certain flooded oilfields, we have further arguments against the above theory of infiltration in the study of the chemical composition of deposit waters from which Mrazec reaches very important conclusions.

The water of petroleum deposits contains, besides sodium chloride, small amounts of iodine, bromine, ammonia, phosphoric acid and sometimes boric acid. The most curious compound is iodine. Salt massifs or fresh waters do not contain iodine. This definitely excludes the formation of deposit waters by the dissolution of salt massifs. The waters occurring in petroleum deposits must be considered as being of fossile origin, and their formation must be correlated somehow with the appearance of oil.

Deposit waters contain on the average 50 grm. iodine per cubic metre; sometimes, as in the Dutch Indies, this concentration might rise even to 135 grm. per cubic metre. The residue of these waters by evaporization contains usually 100–350 grm. iodine per ton, which is a large proportion when compared with Chili saltpetre, the main source of iodine on the earth, which averages 500 grm. per ton iodine.

If the iodine from deposit waters cannot be derived either from fresh water or salt massifs, its origin must be sought elsewhere. Sea water contains only traces of iodine, which cannot be estimated. We find, however, in the sea, some living organisms, especially plants which absorb the small amounts of iodine from sea water and fix it as organic complexes just as do terrestrial animals. Thus certain algæ of the Atlantic, *e.g.* the *Laminaria*, contain 12 grm. of iodine per ton of dry substance, whilst *Macrocystis pyrifera* contains as much as 300 grm. iodine per ton. This property of accummulating iodine might exist in the microscopic sea organisms, which, however, have not been investigated until now. When these organisms were subjected to the process of bituminization, the iodine they contained was transferred to the sea in the ionic form which remained as such in the primary deposits. These waters became the oil waters of to-day.

All these findings enable us to comprehend, in general, the beginnings of the process of bituminization. This process occurred probably in a lagoonal sea isolated from the ocean and endowed with a luxuriant life. When the climate became arid, the waters were evaporated, which explains

the high salt content of the oil-deposit waters. Next, the entire landscape was submerged, and the organic débris (the formation of which will be discussed below) were covered with solid and impervious sediments.[8] McKenzie Taylor[9] has formulated an ingenious theory on the processes regarding the formation of impervious clay deposits.

A much discussed question is that of the source rock in which petroleum originated. It is generally admitted, nowadays, that oil does not occur in the rocks in which it was formed, contrary to the opinion of former authors. Petroleum occurs to-day in psamnitic rocks, porous sandstone rocks or porous limestone, where it has migrated from the substance rocks in which it was formed. Oil has been accumulated in these secondary deposits in certain favourable tectonic elements, in anticlinals and along faults.

Let us now analyse, according to Krejci-Graf,[10] one of the most important oil strata of Roumania—namely, the *Meotic*. The Meotic strata are never composed of clays or other compact rocks, but contain porous sands only. No polybituminous black rocks are found. In general, the Meotic does not contain oil, but the latter may be found in certain privileged positions in the anticlinals, near faults and in the vicinity of salt domes. In the Meotic we find alternating layers of fresh- and salt-water fossils, which proves alternating submersions and elevations of earth's crust, or probably a lagoonal region.

Based on the stratification of conglomerates, it follows that water was moved down to the very bottom, which could not have been very deep. The presence of calcareous mussels on the bottom of the sea shows that the water contained oxygen even at the bottom. Therefore, the reducing medium, so necessary for the formation of oil, as we have seen above, was absent.

The same applies to nearly all the exploitable deposits. Petroleum is secondary in these deposits. It migrated there from other rocks. There are very many proofs which show that petroleum has migrated, so that we shall not insist on this point. Petroleum occurs in different strata—it may be found even at 1000 metres depth. It would be impossible to admit that oil was formed in all these strata of different ages and under very different conditions.

Very interesting from this viewpoint is the fact that the density of Roumanian paraffinous oils increases with the depth of the deposit. Oil contained in the upper strata is richer in light petrol. This phenomenon may be explained by the migration of oil through the porous rocks and by the fact that in this manner the heavy components remain in the lower strata, whilst the light fractions perfuse above. In some cases the loss of the heavy and coloured compounds by filtration is so great that oil occurs in the water-white state,[11] as is the case at the oilfields of Cămpeni, Tețcani and the recently discovered fields at Haimanalele and Margineni. Such oils are found only in the upper strata, and as we go deeper we meet heavier and darker materials, first yellow, then brown and finally black.

This does not apply to the Roumanian asphaltic oils, which differ from the above by their low paraffin content and their richness in superior aromatic hydrocarbons in the lubricating fractions, as well as by a high octane number of the gasoline distilled from them. These asphaltic oils

occur in the form of caps over the paraffinous petroleum strata. In this case, density decreases with the depth, but this phenomenon is not quite general.

In the formation of non-paraffinous oils secondary oxidation by atmospheric oxygen has undoubtedly taken place, as supported by the fact that the waters of these deposits do not contain iodine, and by the high carbon dioxide and gas content, as well as by the high percentage of naphthenic acids. It is possible that during the migration towards the surface the oils, freed in a large measure of their paraffin by filtration and adsorption, might have reached conditions at a given moment when atmospheric oxygen could diffuse to the strata in limited amounts. We must admit, however, that this theory does not explain sufficiently all the differences observed between these oils and the paraffinous ones from which they surely originate, and thus the question needs further investigation.

If we admit that petroleum in the actual deposits is of secondary origin, the question arises as to which is the source rock in which oil originated.[12] It is evident that the migration of oil from this rock could not have been quantitative. Oil is a complex mixture of hydrocarbons, light and heavy. It is to be expected that when migration occurred, a part of the bitumen (the heaviest) should have remained in the source rock. This rock should therefore be polybituminous.

We have seen above that oil deposits occur in psamnitic rocks, *i.e.* composed of macroscopic particles. These could have settled only in a stormy sea down to the bottom, and should be oxygenated. Thus in the formation of psamnitic rocks we do not encounter the hydrogenating conditions which, as we have seen above, are essential to the formation of oil. The source rock of petroleum must have been pellitic, *i.e.* composed of very fine particles of colloidal dimensions, since the sea in which the sedimentation occurred was afterwards transformed into bitumen, and must have been a serene deep sea, and the primary deposits situated far from the shore. The fine mineral particles of the primary deposits can absorb on their surface certain components of bitumen, in accordance with the laws of adsorption. It may be said that the heaviest components and the polymerized molecules are those that are adsorbed best. At the moment when migration occurred the source rock was supersaturated with bitumen. After migration, a certain quantity of bitumen corresponding to saturation should have remained adsorbed on the colloidal particles of the source rock. A rock in order to be considered as source rock of petroleum must not only be rich in bitumen, but should be also saturated with bitumen. We shall expect source rocks to be polybituminous saturated rocks. They must cover a considerable area in order to explain the formation of the neighbouring oil deposits.

These conditions are perfectly fulfilled by certain Disodyllic strata which come up to the surface at Cornu (Prahova district, Roumania). They extend along the Carpathian chain and attain sometimes a thickness of 300 metres. There we find dark coloured or black polybituminous clays or schists and in many places still supersaturated, yielding bitumen if pressure is applied. These rocks contain pyrites and other sulphides, do not contain benthos and calcareous shells, which prove that the bottom waters did not contain oxygen. Rare marine fossils are found, and the salt concentration

is rather high, which shows that they originated in lagoons with an arid climate.

Similar results have been obtained by the research undertaken by the Russian geologist Archangelsk, on the Grosny strata. Beds very rich in organic material were discovered there. The Russian authors consider as possible source rocks of petroleum the strata which exceed 40 kg. permanent organic substance per cubic metre; in rich oilfields this figure reaches even 350 kg. per cubic metre.

## The Mother Substance and its Transformations.

The question of the mother substance of petroleum has been very much discussed, all possible solutions being taken into consideration. These long discussions were crystallized in H. Potonié's saprophele theory, which is too well known to insist upon. Only fermenting mud produced over sufficiently large areas, extending over a long period, may contain sufficient quantities of organic material to explain the formation of the enormous quantities of exploitable oil deposits.[13]

From the apparition of the saprophele theory numerous fresh water muds were investigated in Germany by Potonié [14] as well as marine muds by Trask [15] and other Russian authors (Black Sea).

The results of this research may be summarized as follows: the raw material forming the saprophele is *plankton* and in a smaller degree nekton. Moreover, saprophele may be formed by higher organisms such as algæ (*Phylopora Zostera* and others), which in the Black Sea attain an area of 2700 square kilometres. The vicinity of the poisoned domain of the Black Sea with these huge amounts of plants moved to and fro by the currents renders plausible a sedimentation of these plants under similar conditions as the saprophele.

The body of the organisms which compose the plankton consists mainly of protein and smaller amounts of fat and carbohydrates.

Not every kind of saprophele leads to the formation of a movable liquid bitumen. In most cases, according to local conditions, saprophilites are formed—bituminous schists containing more or less polybitumen or bituminous coal, such as bogheads or Australian Cucherite (kerosene shales).[16]

The formation of liquid bitumen necessitates an abundant plankton, which settles in strictly anærobic conditions, in a medium poisoned by sulphuretted hydrogen, together with relatively small quantities of inorganic material of pellitic nature. Here it is subjected to the action of bacteria living only in the total absence of oxygen.

Such conditions are met with even to-day in the Black Sea.[17] It is well known that the bottom of this Sea is poisoned with sulphuretted hydrogen, which rises slowly, and it is expected that in the distant future life here will disappear completely. The living organisms or cadavers which reach the poisoned level settle down, forming an abundant saprophele.

An interesting study on the Black Sea mud was published in 1932 by Ginsburg-Karagitschewa and Rodionowa.[18] These two Russian authors have examined mud samples from a depth of 900 metres. The mud contained on the average 9–31 per cent. calcium carbonate and 23–35 per cent.

organic substance. Approximately 10 per cent. of the organic substance is soluble in benzene. The solution is green on account of the chlorophyll which has still remained unchanged. On evaporation of the benzene, a bitumen is obtained having a molecular weight of 350–500, consisting mostly of hydrocarbons. Unfortunately, the samples were insufficient to permit a complete study of the bitumen. The results are, however, so promising that the continuation of this difficult and expensive research is much to be desired.

We thus find in the Black Sea very similar conditions to those which should have existed in the seas in which the source rocks of the various oil deposits were sedimented. According to Archangelsk,[19] the Tertiary strata in North Caucasus considered as the source rock of petroleum in that region have about a similar composition as the Black Sea mud. We find here, likewise, signs of sulphuretted hydrogen fermentation.

The transformation suffered by the organic substance of the various dead organisms which settle down to become bitumen is still very little known. According to Engler's classical theory, it is admitted that the mother material (proto-bitumen) undergoes at first a slight change, giving rise to ana-bitumen (a fossilized product) not too different from the mother substance, but much more stable, and capable of resisting the powerful action which follows later on. According to Engler, ana-bitumen undergoes a polymerization giving rise to polybitumen rich in hydrogen and containing probably much oxygen and nitrogen. The transformation of this polybitumen into ecgono-bitumen, *i.e.* petroleum, is a depolymerization process, a breaking of the large molecules and the disproportioning of polybitumen, the intermediate phase of this process being, according to Engler, cata-bitumen.

This theory could not be verified in all its points, and the passage through the polybituminous phase is rather doubtful. Natural polybitumen is found in nature in enormous amounts, and appears to be rather the final product of a complicated and unknown process than the intermediate phase of a process leading from ana-bitumen to ecgono-bitumen. The fact that polybitumen is much more widespread in nature than ecgono-bitumen is due undoubtedly to the fact that the latter, being volatile, was only stored and preserved when isolated by perfectly impervious strata, whilst polybitumen is much more resistant to any kind of influences.

From all these intermeditary products, cata-bitumen is the most uncertain, because no such kinds of bitumen were found in nature which would with certainty correspond to this stage of transformation. On the other hand, the classical conceptions of ana-bitumen have taken a concrete form recently by the study of substances resulting from animal cadavers, when exposed to special conditions, other than the usual. Normally, in the presence of oxygen and water, the organic substances forming the bodies of animals and plants undergo, under the influence of various bacteria, a total decomposition which leads finally to the gases : $CO_2$, $NH_3$ and water.

If, however, from the outset, the cadavers are stored in the total absence of oxygen, a very different kind of decomposition takes place under the influence of certain anærobic bacteria, such as the sulphur bacteria which produce sulphuretted hydrogen. The quantity of gas or soluble substances is smaller, whilst most of the substances of which the cadavers are com-

posed undergo only a slight change, and may be preserved for an indefinite period, even in the primitive form of the cadaver. This has been known since 1785–87, when, on the occasion of excavations effected in Paris at the Cimètière des Innocents, situated in low and flooded ground, several non-putrid cadavers were found composed of a soft white material which was called cadaver-wax. Such old well-preserved cadavers were found even later on several occasions, and the time required for the formation of cadaver-wax was established. Recently, Wasmund [20] has examined critically all known cases of preserved cadavers which have yielded cadaver-wax. The analysis of this material shows that cadaver-wax contains higher free fatty acids and alkaline earth salts of these acids. According to the opinion of some authors, these acids are derived only from the primitive glycerides contained in the cadavers which had undergone a hydrolysis in the presence of water, while the other components of the cadavers, *i.e.* proteins, would yield water-soluble products, and would thus disappear from the vicinity of the cadavers. According to Wasmund (*loc. cit.*) the fatty acids found in the cadaver wax occur in larger amounts than in the original cadavers. Therefore, it must be admitted that a part of the protein is transformed into fatty acids by unknown agencies. The explanation of this problem is of a very great importance for the elucidation of the origin of petroleum. On the other hand, it would be interesting to study the behaviour of the various components of plants and animals, such as proteins and carbohydrates, and especially cellulose under anærobic conditions. In this manner might be established whether only fats or also the other components of animal and plant bodies may pass into the sub-fossile form of cadaver-wax which may be identical to the ana-bitumen of Engler. Very promising experiments in this direction were made by Hecht,[20] who has left various organic materials to rot under water, not, however, in water containing sulphuretted hydrogen. There is no doubt that the first transformation of plant and animal bodies under anærobic conditions are due to bacterial action. A systematic study of these bacteria is therefore imperative. Bacteria causing sulphhydric fermentation which consume sulphuretted hydrogen and store sulphur in their bodies, just as living organisms which store fats in the presence of oxygen, have been known for a long time.

Very interesting and promising are the above-mentioned bacteriologic studies of Ginsburg-Karagischewa and Rodionowa (*loc. cit.*) with mud samples from the Black Sea. From these samples, collected under sterile conditions, cultures were made in various media, whereby growths of tetanos-like bacteria (drumsticks) were obtained which had the following properties: (1) reduce sulphates, *i.e.* sodium and calcium sulphates, giving sulphuretted hydrogen and precipitating black iron sulphide if Fe ions are present; (2) decompose the albumins; during this process $NH_3$ is given off, water-soluble products are formed and combustible gases (methane) are evolved. The evolution of methane is so great in certain parts of the Black Sea (*i.e.* at the Kertsh pass) that methane may be recovered at the surface. Cellulose is transformed into glucose, and the latter into butyric and lactic acids, ethyl alcohol, carbon dioxide and methane; (3) finally, the action on fats is very interesting. The fats are hydrolysed and at the same time the iodine number decreases, whilst the non-saponified fraction

increases. These bacteria have, therefore, a reducing and probably a condensing action. This research was carried out with too small amounts of substance, so that further work in this direction is much to be desired.

The interest of these studies is enhanced by the fact that these two Russian authors have found similar bacteria to those from the bottom of the Black Sea also in the oilfield waters of the Apscheron Peninsula and in the region Naphtalan Grosny and Naftogorsk.

Likewise, Bastin, working independently, has found, at the same time as the Russian authors, similar bacteria in the oilfield waters of Illinois and Kansas.

The fate of the organic material after sedimentation is entirely unknown. During the next phases of evolution of the organic substance it is possible that both chemical and biological changes occur. These phenomena are probably enhanced by the submersion of the strata and by the subsequent increase of temperature. The molecules are then ruptured. The average molecules of ana-bitumen cede their hydrogen to the others which become smaller and richer in hydrogen. This leads to ecgono-bitumen (*i.e.* petroleum). The molecules which have ceded their hydrogen are polymerized and condensed to form that part of the polybitumen which cannot migrate and remains fixed by adsorption to the colloidal particles of the source rock. Between these extremes during this process of disruption molecules of different magnitudes are formed containing different amounts of hydrogen. The formation of the various kinds of molecules depends on local conditions which have not yet been fully explained. Likewise, the catalytic influence of the source rock on this process is still a problem awaiting solution.

From what we have said above, certain precise facts may be gathered from the vast number of theories, which form a comprehensive basis defying any criticism from any kind of scientific investigation. It has been shown that these facts may sometimes be controlled even experimentally, and will probably lead, in the near future, to the complete elucidation of the problem.

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# THE ACTIVITY OF OXYGEN TOWARDS HYDROCARBON MIXTURES WITH A HIGH MOLECULAR WEIGHT.

By H. I. Waterman, J. J. Leendertse and E. C. H. Palm.

The behaviour of oxygen towards hydrocarbons has already been the subject of an extensive research.*

In this field of research two important problems may be distinguished:

(1) the oxygen-stability of hydrocarbons and mixtures of hydrocarbons studied with the intention of preparing hydrocarbon mixtures stable towards oxidation, *e.g.* for lubricants or insulating oils;

(2) the investigation of the products obtained by the oxidation of hydrocarbons and mixtures of hydrocarbons, in special cases with the intention of preparing oxygen containing products of technical importance.

The literature indicates clearly that, in general, the stability of hydrocarbons towards oxygen will not only depend on the chemical structure of the hydrocarbons, but in some cases the stability can be influenced greatly by traces of "impurities." Especially in the case of the natural hydrocarbon mixtures with relatively high molecular weight and of different origin, the structure will vary very much; there may be also a wide difference in the nature and the quantity of the "impurities" in these oils. Therefore, especially in this case, it will be very difficult to solve the problem of oxygen-stability in a general and non-complicated way, although by systematic research some general rules may be found. In studying the nature of the products of the oxidation, it will be found that the conditions of the oxidation have an important effect on the products obtained. As in this case the problem is very complicated, it will be necessary to study each special case separately.

Some general remarks will be given below on the quantity of "sludge" which is formed during the oxidation, under standardized conditions, of several hydrocarbon mixtures with different structures. The authors would have hesitated to communicate the results of these investigations had not a new method been used to identify the chemical nature of the hydrocarbon mixtures.[1] By this method the cyclic character of the oils was defined.

For the determination of the quantity of "sludge" which is formed during the oxidation, the standardized method known as the "Sligh-

* An extensive research on the oxygen stability has been made, *e.g.* by Chernozkukov and by Yamada. This research has proved, *inter alia*, the influence of aromatic compounds and of small amounts of sulphur compounds on the oxygen stability of hydrocarbons and mixtures of hydrocarbons.

Also the work of Ornstein for insulating and lubricating oils may be mentioned here.

During the preparation of this paper there appeared a paper by H. Suida on "Alterung von Schmieröle," *Öl und Kohle* **13** (9–10), March 1937. The conclusions of Suida may be compared with the results obtained by the authors.

oxidation method "[2] has been used. From the large number of oxidation tests described in the literature for lubricating oils, this method was chosen for its simple procedure and for the small quantity of test-oil required. However, a distinct disadvantage of the method is that only the amount of "sludge" formed by the oxidation is determined, and not the total oxygen absorption.

In this investigation about 80 mixtures of hydrocarbons were used, mostly of the gas oil or lubricating oil type. Many of these oils were completely saturated, in most cases by a careful non-destructive catalytic hydrogenation of the unsaturated oils. The hydrogenated mixtures contained practically no other elements besides carbon and hydrogen. The saturated oils were partly derived from natural oils and partly from polymer fractions by the hydrogenation method mentioned above. In several cases the corresponding unsaturated oils were also considered. Several products obtained by the destructive hydrogenation of natural oil fractions and some products obtained by selective extraction (Edeleanu) from natural oil fractions were also used for the "Sligh-test." In some cases partly hydrogenated fractions were investigated for comparison.

## Results of Determinations.

The results of the determinations have been collected in tabular form. The quantity of "sludge" is accurate to about 10 per cent. in those cases where a considerable amount of "sludge" was formed. In some cases (oils no. 9, 17, 19, 20, 78, 80, 85, 86, 88) a blank run had to be made, as these oils were not completely soluble in the standard gasoline used for the precipitation of the "sludge" in the reaction mixtures after the oxidation. In these cases the values mentioned in the table have been obtained by subtracting from the "sludge" numbers found in the experiments the "sludge" values found in the blank run (viz. an experiment analogous with the oxidation test, in which, however, the oxidation itself is omitted. It had been proved before that the "sludge" obtained by the precipitation in the blank run does not have a *special* influence on the result).

In the tables the origin of the oils has been described, in so far as it is known. The refractivity, the density, the specific refractivity, the mean molecular weight (determined by cryoscopic methods) and the aniline point of the oils have also been given. The latter aniline point can be compared with the aniline point read from the diagram for saturated hydrocarbons from the specific refraction determined for the hydrocarbon mixture considered and its mean molecular weight.[1] If there is no difference (or only a small one) between the aniline points of both columns, this fact indicates the complete saturation of the oils. In several cases this saturation has been confirmed by the determination of the specific dispersion $\frac{n_{C'} - n_C}{d} \times 10^4$. In the next two columns the sulphur contents and the specific dispersions have been given. The following columns indicate the percentages of aromatic and naphthenic rings in the hydrocarbon mixtures; these percentages have been calculated in the well-known way,[2] in supposing the presence of condensed six-carbon rings. For the unsaturated oils the

composition in some cases could be deduced from the products obtained after complete non-destructive hydrogenation, in other cases the composition was predicted from the physical constants of the oils as such.[2] By subtracting the sum of the percentages of aromatic and naphthenic rings from 100, the percentage of paraffinic chains can be calculated. The last column in the tables gives the quantity of "sludge" obtained by the oxidation of 10 g. oil (eventually corrected for the "sludge" value from the blank run, see before).

The most important result was obtained with the completely saturated hydrocarbon mixtures. Most of these products had been obtained by careful catalytic hydrogenation of unsaturated oils, and therefore they were probably practically free from elements other than carbon and hydrogen. For this reason, it could be expected that final differences in the oxygen-stability of these hydrocarbon mixtures would be caused mainly by differences in the structure of the hydrocarbons themselves.

However, for all saturated oils the quantity of "sludge" was very low. This was also the case with the oils originating from polymerization of low molecular weight olefines. In the latter oils an important branching will be present (oils 42 and 44). Also the hydrocarbon mixtures 37, 40, 41 and 43, which are not completely saturated, but in which an important branching will also be present, give a very low "sludge" value. For the oils investigated there is no remarkable difference in the "sludge" formation for the saturated oils of a mainly paraffinic structure and of a mainly naphthenic structure. For the oils containing aromatic rings the "sludge" formation is generally greater than for the corresponding completely hydrogenated oils, *e.g.* oil no. 17 gives a "sludge" value 184, the corresponding hydrogenated oil (no. 18) giving only a value 7. Another example is given by the oil no. 78 which produced 175 mg. "sludge," as compared with the corresponding saturated oil no. 63, which gave only 5 mg. "sludge" from 10 g. oil. The "sludge" values show a tendency to increase with increasing percentage of aromatic rings. However, only the word "tendency" may be used, as the results indicate distinctly that the simple determination of the percentage of aromatic rings is not at all sufficient to *predict* the "sludge" value that will be obtained by the oxidation method described above. There are many irregularities which can be explained either by differences in the hydrocarbon structure, or by the presence of small amounts of "impurities," or by both factors. As an example may be mentioned the oils 78 and 85, which both give about 170 mg. "sludge"; oil 78 contained 68 per cent. of aromatic rings, whilst oil 85 did not contain more than 21 per cent. of aromatic rings. As in the complete hydrogenation of the unsaturated oils, not only the unsaturation is removed, but generally also the main percentage of the "impurities," the decrease in the "sludge" values by the complete hydrogenation can be explained by the saturation of the products as well as by the decrease of the amount of "impurities" in the products.

It has been proved that in special cases the "sludge" value can be diminished appreciably even by a *partial* hydrogenation; *e.g.* by the partial hydrogenation of the strongly aromatic oil no. 19, oil 21 has been obtained. Although the latter oil contained as much as 26 per cent.

| Oil number. | Nature of the Oil. | Physical Constants. | | | | | | S %. | $\frac{n_{\sigma'} - n_C}{d} \times 10^4$. | Percentage of Rings. | | "Sludge" in mg./10 g. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $n_D^{15}$. | $d^{20}/_4$. | $\frac{n^2-1}{n^2+2}\frac{1}{d}$ | Molecular Weight. | Aniline Point ° C | | | | | | |
| | | | | | | Observed. | Read from Graph.[a] | | | Aromatic. | Naphthenic. | |
| 1 | Motor oil A | 1·4895 | 0·8811 | 0·3278 | 664 | 122·2° | 131·5° | 0·08 | — | 6 | 15 | 0·6 |
| 2 | ,, ,, B | 1·4935 | 0·8864 | 0·3281 | 592 | 115·7° | 127·5° | 0·11 | — | 8 | 14 | 0·8 |
| 3 | ,, ,, C | 1·5085 | 0·9167 | 0·3255 | 480 | 95·6° | 115·5° | 0·33 | — | 14 | 24 | 9 |
| 4 | Penna oil, distillate fraction I (cathodic light vacuum) | 1·4801 | 0·8641 | 0·3289 | 375 | 97·4° | 110·0° | — | — | 9 | 15 | 16 |
| 5 | ,, ,, ,, ,, II ,, ,, | 1·4817 | 0·8666 | 0·3288 | 425 | 102·9° | 115·5° | — | — | 9 | 13 | 15 |
| 6 | ,, ,, ,, ,, III ,, ,, | 1·4834 | 0·8698 | 0·3286 | 465 | 108·8° | 118·6° | — | — | 7 | 14 | 12·5 |
| 7 | ,, ,, ,, ,, IV ,, ,, | 1·4859 | 0·8741 | 0·3284 | 540 | 113·6° | 124·3° | — | — | 7 | 13 | 8 |
| 8 | ,, ,, ,, ,, V ,, ,, | 1·4898 | 0·8809 | 0·3281 | 640 | 120·0° | 130·6° | — | — | 7 | 13 | 3 |
| 9 | Fraction from distillation of Borneo oil, raw material of extraction experiments | 1·5728 | 1·0084 | 0·3267 | 286 | 16 to 17 | 93 | 0·48 | — | ca. 51 | ca. 19 | 81 (9)[b] |
| 10 | Fraction from distillation of Borneo oil, raw material after hydrogenation | 1·4976 | 0·9251 | 0·3167 | 300 | 78·4 | 80·5 | — | 156 | — | 70 | 5 |
| 11 | Refined product from oil no. 9, extracting liquid $SO_2$ | 1·5120 | 0·9350 | 0·3209 | 348 | 70·8 | 95 | 0·25 | — | 14 | 43 | 45 |
| 12 | ,, ,, ,, ,, no. 9, extracting liquid $SO_2$ after hydrogenation | 1·4960 | 0·9172 | 0·3186 | 344 | 88·2 | 90·5 | — | 158 | — | 59 | 2 |
| 13 | Refined product from oil no. 9, extracting liquid $SO_2+C_2H_3Cl$ | 1·5079 | 0·9292 | 0·3208 | 359 | 75·4 | 96 | 0·23 | — | 13 | 45 | 29 |
| 14 | ,, ,, ,, ,, no. 9, extracting liquid $SO_2+C_2H_3Cl$ after hydrogenation | 1·4948 | 0·9150 | 0·3186 | 357 | 91·0 | 92·5 | — | 156 | — | 58 | 1 |
| 15 | Refined product from oil no. 9, extracting liquid $SO_2+C_6H_6$ | 1·5118 | 0·9343 | 0·3211 | 327 | 71·8 | 92 | 0·24 | — | 14 | 43 | 54 |
| 16 | ,, ,, ,, ,, no. 9, extracting liquid $SO_2+C_6H_6$ after hydrogenation | 1·4949 | 0·9155 | 0·3184 | 374 | 88·8 | 93 | — | 156 | — | 57 | 2 |
| 17 | Extract from oil no. 9, extracting liquid $SO_2$ | 1·59 | 1·0351 | — | 274 | < 0 | — | 0·54 | — | > 62 | < 10 | 184 (76)[b] |
| 18 | ,, ,, ,, no. 9, extracting liquid $SO_2$ after hydrogenation | 1·5014 | 0·9317 | 0·3165 | 286 | 74·2 | 78 | — | 158 | — | 72 | 7 |
| 19 | Extract from oil no. 9, extracting liquid $SO_2+C_2H_3Cl$ | 1·59 | 1·0281 | — | 269 | < 0 | — | 0·58 | — | — | — | 164 (84)[b] |
| 20 | ,, ,, ,, no. 9, extracting liquid $SO_2+C_6H_6$ | 1·58 | 1·0269 | — | 278 | < 0 | — | 0·56 | — | — | — | 160 (90)[b] |
| 21 | ,, ,, ,, no. 9, extracting liquid $SO_2+C_2H_3Cl$ (after partial hydrogenation) | 1·5251 | 0·9621 | 0·3186 | 275 | 40·2 | 78·5 | — | — | 26 | 57 | 6 |

| Oil number. | Nature of the Oil. | Physical Constants. | | | | | | S %. | $\frac{n_D' - n_D}{d} \times 10^4$. | Percentage of Rings. | | "Sludge" in mg./10 g. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $n_D^{t°}$. | $d^{t°}/_4$. | $\frac{n^2-1}{n^2+2}\frac{1}{d}$ | Molecular Weight. | Aniline Point °C | | | | | | |
| | | | | | | Observed. | Read from Graph.[a] | | | Aromatic. | Naphthenic. | |
| 23 | Refined product from Borneo oil, after complete hydrogenation | 1·4843 (50°) | 0·8962 (50°) | 0·3186 (20°) | 373 | 96·4 | 95 | — | — | — | 56 | 2 |
| 24 | Extract from Borneo oil, 70 per cent. fraction of the raw material [c] | 1·6024 | 1·0434 | 0·3289 | 325 | < 0 | 103 | — | — | 56 | 13 | 58 |
| 25 | Extract from Borneo oil, 70 per cent. fraction of the raw material after hydrogenation [c] | 1·5037 | 0·9363 | 0·3161 | 334 | 82·8 | 86 | — | 155 | — | 69 | 12 |
| 26 | Extract from Borneo oil, 70 per cent. fraction of the berginisation experiment [c] | 1·610 | 1·0529 | 0·3292 | 312 | < 0 | 101 | — | — | 60 | 12 | 42 |
| 27 | Extract from Borneo oil, 70 per cent. fraction of the berginisation experiment after hydrogenation [c] | 1·5054 | 0·9404 | 0·3155 | 324 | 78·5 | 83 | — | 156 | — | 72 | 8 |
| 28 | Extract from Borneo oil, 70 per cent. fraction of the nickel experiment [c] | 1·5865 | 1·0315 | 0·3256 | 295 | < 0 | 93 | — | — | 52 | 21 | 20 |
| 29 | Extract from Borneo oil, 30 per cent. fraction of the raw material [c] | 1·5921 | 1·0269 | 0·3296 | 273 | −15 | 95 | — | — | 59 | 10 | 52 |
| 30 | Extract from Borneo oil, 30 per cent. fraction of the raw material after hydrogenation [c] | 1·4896 | 0·9082 | 0·3181 | 255 | 71·8 | 74 | — | — | — | 69 | — |
| 31 | Refined product from Borneo oil, 70 per cent. fraction of the berginization experiment [c] | 1·5189 (30°) | 0·9458 (30°) | 0·3209 (30°) | 395 | 75·4 | 100 | — | — | 17 | 41 | 17 |
| 32 | Refined product from Borneo oil, 70 per cent. fraction of the berginization experiment after hydrogenation [c] | 1·4990 | 0·9232 | 0·3180 | 396 | 95·8 | 97 | — | 151 | — | 58 | 2 |
| 33 | Refined product from Borneo oil, 70 per cent. fraction of the molybdenum experiment [c] | 1·5144 | 0·9432 | 0·3194 | 394 | 78·8 | 98 | — | — | 14 | 46 | 3 |
| 34 | Refined product from Borneo oil, 70 per cent. fraction of the molybdenum experiment after hydrogenation [c] | 1·4994 | 0·9252 | 0·3176 | 395 | 95·1 | 96 | — | 152 | — | 60 | 2 |
| 35 | Refined product from Borneo oil, 70 per cent. fraction of the nickel experiment [c] | 1·4941 | 0·9019 | 0·3228 | 297 | 76·7 | 89 | — | — | 10 | 41 | 33 |
| 36 | Refined product from Borneo oil, 70 per cent. fraction of the nickel experiment after hydrogenation [c] | 1·4823 | 0·8887 | 0·3214 | 301 | 88·7 | 88 | — | 152 | — | 51 | 2 |

| Oil number. | Nature of the Oil. | Physical Constants. | | | | | | S %. | Percentage of Rings. | | "Sludge" in mg./10 g. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $n_D^{15}$. | $d^{15}/_4$. | $\frac{n^2-1}{n^2+2}\frac{1}{d}$ | Molecular Weight. | Aniline Point. Observed. | Aniline Point. Read from Graph.[a] | | Aromatic. | Naphthenic. | |
| 37 | Polymer fraction of *iso*butene (catalyst $AlCl_3$, temperature 0–20° C.) | 1·4632 | 0·8286 | 0·3325 | 430 | 105 | 121 | 0 | — | — | 0·2 |
| 38 | ,, ,, ,, hexadecene (catalyst $BF_3$)[d] | 1·4666 | 0·8334 | 0·3327 | 766 | 136·4 | ca. 145 | — | 0 | 0 | 1 |
| 39 | ,, ,, ,, hexadecene (catalyst $BF_3$) after hydrogenation[d] | 1·4628 | 0·8294 | 0·3320 | 728 | 140·6 | 140·5 | — | 0 | 0 | 1 |
| 40 | ,, ,, ,, ethylene (i, catalyst $AlCl_3$, temperature 125–150° C.)[e] | 1·4733 | 0·8496 | 0·3304 | 335 | 89·2 | 106 | — | — | — | 0·5 |
| 41 | ,, ,, ,, ethylene (j, catalyst $AlCl_3$, temperature 125–150° C.)[e] | 1·4821 | 0·8660 | 0·3293 | 417 | 95·7 | 115 | — | — | — | 1 |
| 42 | ,, ,, ,, ethylene (j, catalyst $AlCl_3$, temperature 125–150° C.) after partial hydrogenation[e] | 1·4730 | 0·8534 | 0·3287 | 372 | 99·2 | 109·5 | — | — | — | 1 |
| 43 | Polymer fraction of ethylene (k, catalyst $AlCl_3$, temperature 125–150° C.)[e] | 1·4908 | 0·8834 | 0·3277 | 587 | 109·7 | 126 | — | — | — | 2 |
| 44 | ,, ,, ,, ethylene (k, catalyst $AlCl_3$, temperature 125–150° C.) after partial hydrogenation[e] | 1·4830 | 0·8721 | 0·3275 | 524 | 112·9 | 121·5 | — | — | — | 0·1 |
| 45 | Distillate fraction I from Borneo oil (cathodic light vacuum)[f] | 1·5654 | 1·0005 | 0·3257 | 287 | 20·2 | 92 | — | 49 | 22 | 42 |
| 46 | ,, ,, II ,, ,, ,, ,, ,,[f] | 1·5690 | 1·0048 | 0·3261 | 320 | 26·2 | 98 | — | 48 | 21 | 38 |
| 47 | ,, ,, III ,, ,, ,, ,, ,,[f] | 1·5668 | 1·0033 | 0·3255 | 336 | 32·5 | 99 | — | 45 | 23 | 39 |
| 48 | ,, ,, IV ,, ,, ,, ,, ,,[f] | 1·5640 | 1·0005 | 0·3251 | 354 | 35·0 | 101·5 | — | 45 | 23 | 47 |
| 49 | ,, ,, V ,, ,, ,, ,, ,,[f] | 1·5610 | 0·9978 | 0·3245 | 377 | 43·8 | 104 | — | 41 | 24 | 45 |
| 51 | (Oil derived from oil no. 76) | 1·4736 | 0·8546 | 0·3286 | 1263 | 151·8 | — | — | — | — | 1 |
| 52 | | 1·4612 | 0·8313 | 0·3302 | 450 | 116·7 | 120 | — | 0 | 11 | 1 |
| 53 | | 1·4782 | 0·8692 | 0·3246 | 425 | 110·6 | 110 | — | 0 | 32 | 1 |
| 54 | | 1·4770 | 0·8728 | 0·3237 | 375 | 99·6 | 102·5 | — | 0 | 38 | 1 |
| 55 | | 1·4759 | 0·8680 | 0·3249 | 452 | 111·1 | 112·5 | — | 0 | 30 | 1 |
| 56 | | 1·4742 | 0·8638 | 0·3255 | 449 | 110·6 | 113 | — | 0 | 28 | 2 |
| 57 | | 1·4750 | 0·8632 | 0·3262 | 511 | 121 | 119 | — | 0 | 24 | 1 |
| 58 | (Oil derived from oil no. 77) | 1·4798 | 0·8765 | 0·3240 | 450 | 110·8 | 111 | — | 0 | 34 | 0·4 |
| 59 | | 1·4700 | 0·8516 | 0·3276 | 446 | 116·7 | 115·5 | — | 0 | 20 | 0·4 |
| 62 | | 1·5010 | 0·9267 | 0·3179 | 410 | 96·0 | 98 | — | 0 | 58 | 3 |
| 63 | (Oil derived from oil no. 78) | 1·4879 | 0·9036 | 0·3188 | 254 | 72·8 | 75 | — | 0 | 65 | 5 |
| 64 | (Oil derived from oil no. 79) | 1·5007 | 0·9278 | 0·3174 | 314 | 83·2 | 84 | — | 0 | 65 | 8 |
| 65 | | 1·4795 | 0·8745 | 0·3246 | 511 | 118·9 | 117 | — | 0 | 30 | 0·6 |
| 66 | | 1·4816 | 0·8767 | 0·3250 | 645 | 127·8 | 127·5 | — | 0 | 25 | 0·2 |
| 68 | | 1·4620 | 0·8303 | 0·3311 | 490 | 124·4 | 123·5 | — | 0 | 7 | 0·2 |
| 75 | (Oil derived from oil no. 80) | 1·4858 | 0·8932 | 0·3213 | 339 | 94·0 | 94 | — | 0 | 49 | 0·7 |

Natural oils of different origin after complete hydrogenation

| Oil number. | Nature of the Oil. | Physical Constants. | | | | | | Percentage of Rings. | | "Sludge" in mg./10 g. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $n_D^{20}$. | $d^{20}/_4$. | $\frac{n^2-1}{n^2+2}\frac{1}{d}$ | Molecular Weight. | Aniline Point. | | Aromatic. | Naphthenic. | |
| | | | | | | Observed. | Read from Graph.[a] | | | |
| 76 | Natural oils of different origin | 1·4877 | 0·8760 | 0·3287 | 512 | 111·8 | 122·5 | 7 | 13 | 7 |
| 77 | | 1·480 (4) | 0·8653 | 0·3285 | 453 | 107 | 117 | 7 | 16 | 43 |
| 78 | | 1·581 | 1·0105 | 0·3298 | 250 | −10 | 90 | 68 | 7 | 175 (40)[b] |
| 79 | | 1·5488 | 0·9799 | 0·3245 | 310 | 39·0 | 94 | 37 | 29 | 54 |
| 80 | | 1·5251 | 0·9419 | 0·3254 | 334 | 62·0 | 99 | 25 | 28 | 128 (6)[b] |
| 81 | | 1·4902 | 0·8857 | 0·3265 | 564 | 114·1 | 123 | 6 | 22 | 2 |
| 82 | | 1·5217 | 0·9375 | 0·3252 | — | 76·4 | — | — | — | 32 |
| 83 | | 1·5024 | 0·9114 | 0·3240 | 482 | 100·4 | 114 | 9 | 31 | 36 |
| 84 | | 1·4997 | 0·9074 | 0·3240 | 427 | 96·3 | 109 | 9 | 32 | 27 |
| 85 | | 1·525 | 0·9487 | 0·3230 | 428 | ca. 77 | 107·5 | 21 | 33 | 170 (34)[b] |
| 86 | | 1·528 (2) | 0·9359 | 0·3291 | 296 | 62·3 | 98 | 24 | 17 | 103 (9)[b] |
| 87 | | 1·4868 (40°) | 0·8722 (40°) | 0·3296 | 331 | 83·8 | 103 | 13 | 17 | 86 |
| | | | | 0·3291 (20°) | | | | | | |
| 88 | | 1·5220 | 0·9350 | 0·3262 | 352 | 64·6 | 103 | 26 | 24 | 152 (3)[b] |
| 90 | | 1·4972 | 0·9022 | 0·3244 | 460 | 93·8 | 112·5 | 13 | 29 | 3 |
| 91 | | 1·5188 | 0·9313 | 0·3258 | 376 | 73·0 | 105 | 22 | 24 | 41 |
| 92 | | 1·4929 | 0·8926 | 0·3255 | 473 | 101·6 | 115 | 9 | 28 | 40 |

[a] Aniline point corresponding with the specific refractivity and the molecular weight mentioned in the table, read in the graph for saturated hydrocarbons.
[b] The values in parentheses mean the "sludge" values observed in the blank run.
[c] H. I. Waterman, J. J. Leendertse and G. van der Neut, *J.I.P.T.*, 1935, **21**, 816.
[d] H. I. Waterman and J. J. Leendertse, *Trans. Faraday Soc.*, 1936, **32**, 251.
[e] H. I. Waterman and A. J. Tulleners, *Chimie et Industrie*, 1933, **29**, 496; see also thesis A. J. Tulleners, Delft, 1933, and *Trans. Faraday. Soc., l. c.*
[f] H. I. Waterman, P. C. Kruyff, W. J. K. Schönlau and A. J. Tulleners, *J.I.P.T.*, 1934, **20**, 159.

of aromatic rings, the "sludge" value had decreased from 164 to 6 mg.

Two series of experiments have been carried out from which the influence of the molecular weight on the "sludge" formation in this special case may be deduced. The series of oils 4–8 and 45–49 were hydrocarbon mixtures with increasing molecular weight obtained by distillation from one and the same raw material; for the oils 4–8 the raw material was a Penna oil, for the oils 45–49 the raw material was a Borneo oil. In the case of the Penna oil the percentage of aromatic and naphthenic rings did not change much with increasing molecular weight of the fractions; the "sludge" value, however, shows a tendency to decrease with increase of the molecular weight. In the case of the Borneo oil fractions there is not an appreciable regular change of the "sludge" value with the change in molecular weight for the range that has been investigated.

It has already been stated that in determining the "sludge" value of oils in the way described above, only one of the products that can be formed during the oxidation experiment is found. Meanwhile it has been proved that in definite cases in which the "sludge" value had been found to be very low, oxygen had been absorbed for the production of oxygen-containing compounds which were soluble in the oil. The latter fact could be deduced from the values for the acid-number and the saponification number of the products after the oxidation. Chebotar[3] had already directed attention to the possibility that readily oxidizable oils in special cases may give a very low "sludge" value in using the Sligh-test. The latter results indicate distinctly the danger of using an indirect method such as the Sligh-test for judging the total oxygen *stability* of oils.

*References.*

[1] J. C. Vlugter, H. I. Waterman and H. A. van Westen, *J.I.P.T.*, 1932, **18**, 735; completed and revised in *ibid.*, 1935, **21**, 661, 701. See also J. C. Vlugter, Thesis, Delft, 1932.

[2] *Proc. A.S.T.M.*, 1927, **27**, 460. The revised method given in *Proc. A.S.T.M.*, 1935, **35**, 333, does not differ much from the first one.

[3] L. P. Chebotar, *J.I.P.T.*, 1934, **20**, 168.

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*May*, 1937.

# THE ADSORPTION OF BITUMENS BY ROAD AGGREGATES.*

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## Introduction.

There are so many factors affecting the design of asphalt mixtures that it is impossible to estimate, by reference to the usual tests to which the individual constituents are subjected, what results may be produced in mixtures in which they are combined in definite proportions. One of the important factors which distinctly influences the individual constituents and directly affects the mechanical properties of the final mixture has remained practically unrecognized outside the laboratory and insufficiently and vaguely comprehended within it. This factor is the phenomenon of adsorption.

It has been frequently observed that different kinds of road aggregates exhibit a markedly preferential affinity towards certain types of bitumens—for example, Penmaenmawr stone has greater "bitumen-carrying capacity" than Mountsorrel stone. This has never been fully and scientifically explained.

The object of this paper is to investigate this preferential behaviour and explain it in terms of adsorptive capacity of the aggregate.

After studying the published work on the subject, it would appear (see Bibliography [1-8]) that the measurement of adsorption calls for two fundamental considerations :—

A. Accurate determination of the surface area of aggregate;
B. Exact determination of the quantity of adsorbed bitumen.

The value of the results of such an investigation depends entirely on the accuracy of the methods for determining A and B.

For the former it was finally decided to use a photoelectric turbidimeter developed by Broome embodying the same principles as Wagner's turbidimeter.[9]

This method utilizes a relationship between the degree of turbidity of a suspension and the surface area of the dispersed solid, together with Stokes' law predicting the rate of fall of spherical particles through a viscous medium. The apparatus consists essentially of a source of light of constant intensity, which passes through a suspension of the powdered rock to be tested into a sensitive photoelectric cell. The current generated in the cell is measured with a microammeter, and the indicated reading is a measure of the turbidity of the suspension. General considerations have indicated that turbidity is a measure of the surface area of a suspension, and that change in turbidity due to settling of the suspended material is a measure of distribution of that surface area.

* Paper received March 3rd, 1937.

### Exact Determination of Quantity of Bitumen Adsorbed.

Having discussed the question of surface areas, the second important factor is the exact determination of the quantity of bitumen adsorbed. This can be determined by :

1. Chemical methods ;
2. Measurement of change of electrical conductivity ;
3. Measurement of colour of solution.

After careful consideration and study of the available literature, it was felt that the most suitable method was a colorimetric one.

Such an estimation is a delicate process, and the errors involved by the human factor in visual estimation of colour are far too numerous to guarantee accuracy of results. The human eye is notoriously unreliable so far as colour comparisons are concerned. It is a well-known fact that no two individuals react in exactly the same way to colour impressions. Even the same individual may vary markedly in his relative evaluating of colour. The reason for this lies in the fact that colour observations, involving not only physical processes, but also physiological and psychological phenomena, are not governed by simple scientific laws. This has been remarked by several workers on colorimetric estimation, and was referred to as early as 1910 by Knapp [9] and quite recently by Broome.[10] A photoelectric apparatus, known as a Panchrometer,[17] was therefore employed, with the kind permission of the Limmer Trinidad Lake Asphalt Co., Ltd.

### Aggregates and Fillers Used.

The investigation has been confined to six types of road aggregates and one asphaltic bitumen.

*Aggregates Used.*

(1) Penmaenmawr stone ;
(2) Mountsorrel stone ;
(3) Quartzite stone ;
(4) Limestone filler ;
(5) Delafilla ;
(6) Portland Cement filler.

(1) Penmaenmawr stone is one of the excellent types of road stones which are used both as large aggregate and as filler. Penmaenmawr stone has been classified as a quartz-enstatite-diabase. Principal minerals in this stone are : micropegamatite, enstatite, augite, quartz, and iron ore.

(2) Mountsorrel granite was particularly included in the selected aggregates because, although it compares favourably with Penmaenmawr stone in its chemical and mineralogical compositions and physical tests, it is markedly different in texture and crystal structure from the Penmaenmawr stone. Chief minerals in Mountsorrel granite are : quartz, plagioclase, potash feldspar, chloritized biotite, sphene, calcite, and sericite.

(3) Quartzite : A stone of pinkish colour composed almost entirely of quartz grains and a few of biotite. It is one of the lesser-known road aggregates. Quarry : Leigh-on-Mendip.

(4) Limestone filler: This filler is composed mainly of calcite, and is very largely used as a filling material by asphalt manufacturers. Quarry: Leigh-on-Mendip.

(5) Delafilla: A well-known type of slate filler from Delabole, Cornwall. Microscopic examination indicates presence of minute fibres of sericite and tiny grains of quartz.

(6) Portland cement filler: This is of very particular interest, in that it has been highly recommended in B.S.S. No. 594 (1935).

Bitumen: The bitumen used is marketed under the trade name of Petmex, Grade 4. It is manufactured from a Mexican crude. There was no particular reason for selecting this bitumen. A limited number of tests were also carried out on Mexphalte "E," a bitumen made from a Venezuelan crude.

The aggregates (excepting the fillers) were obtained in $\frac{1}{8}$-inch to dust form for adsorption tests; only material passing 300-mesh sieve was used, the object being to obtain as large a surface area per gram of material as possible.

## Determination of Particle Size.

The experimental work in this section deals with a detailed description of the test procedure, calculations and principles involved for determining particle size and surface area of Mountsorrel powdered aggregate on the photoelectric turbidimeter. Particle size and surface area for the other aggregates used were determined in the same way.

*Test Procedure*: One gram of powdered granite passing a standard 300-mesh sieve previously heated in an electric oven at a constant temperature of 110° C., and subsequently cooled in a desiccator, is placed in a test-tube with about 10 c.c. of water-white, white-spirit and 3 drops of oleic acid are added. (Oleic acid is added, since it is a suitable dispersing agent and has little effect on the viscosity of the suspending material.) The whole is vigorously shaken for about 5 minutes and kept over-night to ensure perfect wetting of the particles. The lamp of the turbidimeter is switched on and the intensity of light adjusted by means of the rheostat to record 5 microamperes with a clear solution of white spirit in the settling-tank. Having fixed the intensity of light, the test-tube containing the sample is vigorously shaken and its contents are washed into the settling-tank with further quantities of clear white spirit. The tank is filled to a constant height of 37 cm. for all tests. The tank is then steadily shaken for three minutes and placed in the proper position in the path of the light-beam. A timing-clock is started at the instant shaking of the tank is stopped, and microammeter readings are taken at specified intervals of time, according to the limits of the paricle-size determination required.

The principles involved are based on Stokes's law for falling particles and Kohn's analysis of suspensions.[15] Full details of the calculations and the derivation of the formulæ used are given by Broome,[18] whose work is a modification of that of Wagner.[8]

As the general tendency of all forms of settlement apparatus is to yield a slightly coarser grading, due to the unavoidable error of some of the fine particles being pushed down by the coarse ones, an attempt was made to minimize this error. Two check analyses were carried out on the turbidi-

meter, following the same test procedure as described above, and the one yielding the finest grading was taken into account for determining true surface area.

For example, in the case of Mountsorrel the original analysis showed that the percentage by weight of the fraction below 10 microns was 23·84, the corresponding figures in the first and second checks being 23·16, 22·69. Therefore, the surface area determined in the original analysis was regarded

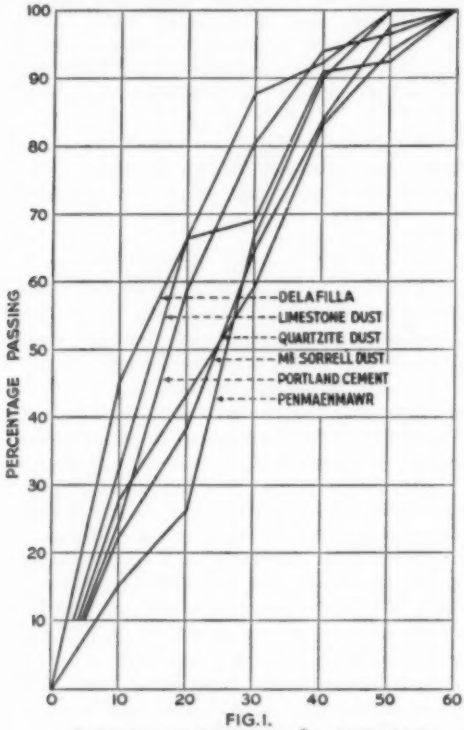


FIG. 1.

as the true surface area for 1 gram of Mountsorrel powdered aggregate. The fraction below 10 microns was considered as the criterion for the relative fineness of the grading of a powder because it comprises the highest percentage of the total surface area per gram (62·24 per cent. in the case of Mountsorrel). See Fig. 1.

## Preliminary Adsorption Tests on a Photobitometer.

While the panchrometer was still in the final stages of its design, a set of preliminary adsorption tests was carried out on a photobitometer.[19] This is essentially a photoelectric bitumen estimating apparatus developed by the

Research Laboratories of the Limmer and Trinidad Lake Asphalt Co., Ltd. It was kindly loaned by the Hutchinson Testing Apparatus Co., Ltd.

TABLE I.

Aggregate: Mountsorrel Granite Dust ex Mountsorrel Granite Co., Ltd.

True Specific Gravity: 2·688.

Size Distribution :—

| Fraction. | Weight Percentage. |
|---|---|
| Minus–10 microns | 23·84 |
| 10–15 „ | 6·70 |
| 15–20 „ | 7·55 |
| 20–25 „ | 3·86 |
| 25–30 „ | 22·90 |
| 30–35 „ | 3·73 |
| 35–40 „ | 14·70 |
| 40–45 „ | 8·62 |
| 45–50 „ | 5·90 |
| 50–55 „ | 2·20 |
| 55–60 „ | nil |

Surface Area :—

| Fraction. | Sq. cms. | Percentage of Total Surface. |
|---|---|---|
| Minus–10 microns | 1052·4 | 62·24 |
| 10–15 „ | 120·0 | 7·13 |
| 15–20 „ | 97·00 | 5·74 |
| 20–25 „ | 38·50 | 2·28 |
| 25–30 „ | 186·00 | 11·00 |
| 30–35 „ | 25·60 | 1·51 |
| 35–40 „ | 88·00 | 5·21 |
| 40–45 „ | 45·50 | 2·70 |
| 45–50 „ | 27·70 | 1·64 |
| 50–55 „ | 9·30 | 0·55 |
| 55–60 „ | nil | nil |

Total surface area per 1 gram. = 1690 sq. cm.

TABLE II.

| Fraction. | Weight Per Cent. Passing. | | | | | |
|---|---|---|---|---|---|---|
| | Delafilla. | Limestone. | Quartzite. | Mountsorrel. | Portland. | Pen. |
| Minus— | | | | | | |
| 10 microns | 44·91 | 32·7 | 27·94 | 23·84 | 25·73 | 15·05 |
| 20 „ | 66·21 | 67·6 | 43·94 | 38·09 | 58·98 | 26·75 |
| 30 „ | 68·98 | 88·4 | 59·79 | 64·85 | 81·98 | 65·65 |
| 40 „ | 90·54 | 92·55 | 83·14 | 83·28 | 94·76 | 91·40 |
| 50 „ | 93·38 | 100·00 | 94·92 | 97·80 | 97·09 | 100·00 |
| 60 „ | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

In its design and component parts the photobitometer is exactly like the photoelectric turbidimeter described previously, the only difference being that instead of a settling-tank, a hollow glass slide containing a bitumen

solution is interposed in the path of light. The reading on the ammeter therefore gives a measure of the concentration of the solution in the slide.

### The Use of the Panchrometer for Measuring Adsorption.

The first series of tests on the panchrometer was carried out with a view to determining the colour of the adsorptive before and after adsorption, "quantitatively," that is, the depth of the colour of the bitumen solution was measured (as on the photobitometer) rather than the quality of the colour (described in later pages).

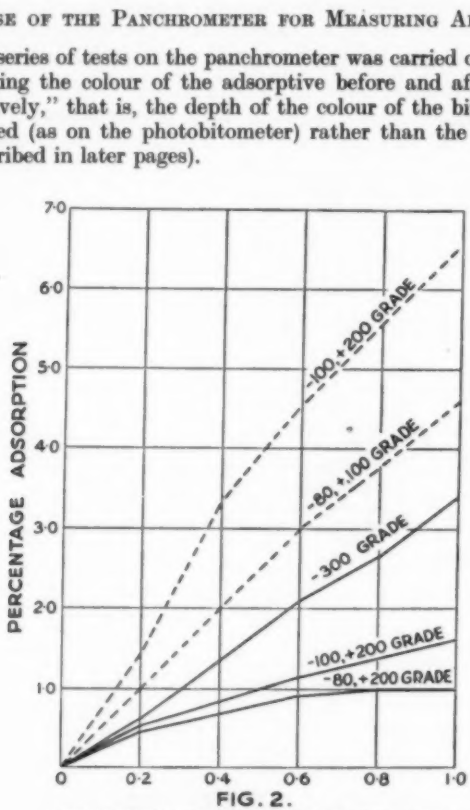


FIG. 2.

Actually seven concentrations of Petmex bitumen varying from 0·2 to 2·0 grams per litre were tested. Results of their transmission values are shown. These were plotted against their corresponding concentrations, and from the resulting curve unknown concentrations corresponding to known transmission values of any solution of Petmex bitumen within the range of zero to 2 grams per litre concentration could be determined. It must be mentioned that white light was used during these tests, and for this purpose the diameter of the light-beam was reduced to 1 millimetre by means of a special "stop" owing to the high sensitivity of the photocell equipment to white light.

For measuring the quantity of bitumen adsorbed by the six aggregates at different concentrations, a weight proportional to an arbitrary unit of

10,000 cm.$^2$ surface area was taken in each case. Thus, whereas in the case of Penmaenmawr 7·522 grams were taken with every 100 c.c. of the bitumen solution, only 4·0 grams were taken in the case of Delafilla.

In accordance with this procedure three grades of limestone were treated with five different concentrations of bitumen solution, and the amount of bitumen adsorbed at each concentration was determined. The results are shown in Fig. 2. Another set of figures was obtained using a 3000-r.p.m. centrifuge instead of a No. 5 Whatman filter-paper. These latter results are shown by dotted lines in Fig. 2, and by comparison it will be seen that the use of filter-paper as a means of separating the mineral matter from the mixture considerably exaggerates the apparent adsorption capacity of the filler. Thus, for example, with 80/100-mesh grade and a concentration of 1 gram per litre, the use of filter paper increases the percentage adsorption figure from 1·0 to 4·6 per cent.

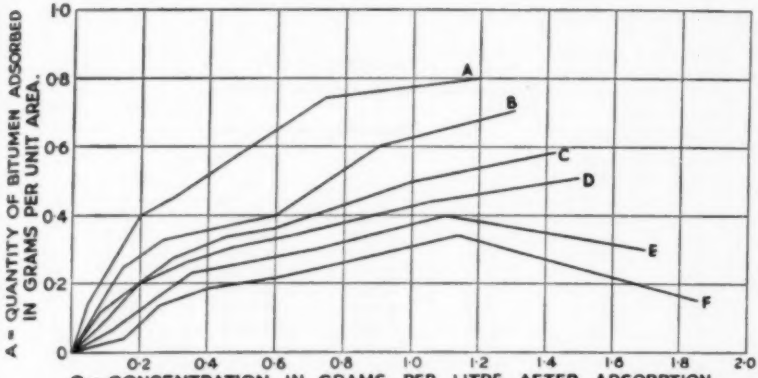


FIG.3.

ADSORPTION ISOTHERMS OF (A) PENMAENMAWR, (B) DELAFILLA, (C) QUARTZITE, (D) MJ SORRELL, (E) LIMESTONE, (F) PORTLAND CEMENT, WITH 'PETMEX' (MEXICAN) BITUMEN.

Data obtained from these tests are shown in Table IV, and graphically illustrated in Figs. 2 and 3. Fig. 3 is of particular importance, in that it shows graphically the variations in adsorption at different concentrations according to Freundlich's equation of adsorption isotherms. This equation is mathematically expressed as follows: $a = kc\frac{1}{n}$, where $a$ = quantity of bitumen adsorbed per unit area; $c$ = concentration of the bitumen solution after adsorption; and $k$ and $n$ are constants depending on the characteristics of the bitumen and the aggregate.

The constant $\frac{1}{n}$ is called the adsorption exponent, whilst $k$ represents that quantity of bitumen adsorbed found when $c = 1$. The formula has no theoretical basis, but was derived by Freundlich empirically from experimental results.

Results on Table V and adsorption isotherms in Fig. 3 show that in the

order of their adsorptive capacity the aggregates experimented upon can be written down as :—

(1) Penmaenmawr stone;
(2) Delafilla;
(3) Quartzite stone;
(4) Mountsorrel stone;
(5) Limestone filler;
(6) Portland cement.

Another interesting point of note is that adsorptive capacity increases with concentration to a limit, beyond which it shows a tendency to diminish with increasing concentration. This is particularly noticed in the case of limestone and Portland cement. This is in no way an indication that adsorption ceases to exist at high concentrations. The explanation lies in the fact that at higher concentrations the solvent plays an important part and re-dissolves some of the adsorbed bitumen.

TABLE III.

*Petmex Bitumen in Benzene Solutions.*

| Concentration, in gms./litre. | Transmission, in volts. | | | |
|---|---|---|---|---|
| | 1. | 2. | 3. | Mean. |
| 2·0 | 0·0500 | 0·0500 | 0·0500 | 0·0500 |
| 1·5 | 0·0627 | 0·0629 | 0·0634 | 0·0630 |
| 1·0 | 0·1000 | 0·1000 | 0·1000 | 0·1000 |
| 0·8 | 0·1161 | 0·1154 | 0·1162 | 0·1159 |
| 0·6 | 0·1400 | 0·1400 | 0·1400 | 0·1400 |
| 0·4 | 0·1660 | 0·1655 | 0·1653 | 0·1656 |
| 0·2 | 0·2000 | 0·2000 | 0·2000 | 0·2000 |

TABLE IV.

| | | Concentration, in grams/litre. | | | | | | | Specific Gravity. | Surface Area, sq. cm./gm. | Weight Equivalent per 10,000 cm.² |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2. | 1·5. | 1·0. | 0·8. | 0·6. | 0·4. | 0·2. | | | |
| Penmaenmawr Granite | c. | 1·2 | 0·75 | 0·45 | 0·33 | 0·20 | 0·12 | 0·04 | 2·780 | 1330 | 7·522 |
| | a. | 0·8 | 0·75 | 0·55 | 0·47 | 0·40 | 0·28 | 0·16 | | | |
| Quartzite | c. | 1·41 | 1·00 | 0·62 | 0·45 | 0·31 | 0·19 | 0·07 | 2·681 | 1870 | 5·347 |
| | a. | 0·59 | 0·50 | 0·38 | 0·35 | 0·29 | 0·21 | 0·13 | | | |
| Delafilla | c. | 1·29 | 0·90 | 0·60 | 0·42 | 0·26 | 0·15 | 0·06 | 2·690 | 2500 | 4·000 |
| | a. | 0·71 | 0·60 | 0·40 | 0·38 | 0·34 | 0·25 | 0·14 | | | |
| Mountsorre Granite | c. | 1·50 | 1·05 | 0·65 | 0·48 | 0·33 | 0·20 | 0·09 | 2·688 | 1690 | 5·915 |
| | a. | 0·50 | 0·45 | 0·35 | 0·32 | 0·27 | 0·20 | 0·11 | | | |
| Mendip Limestone | c. | 1·70 | 1·10 | 0·70 | 0·53 | 0·37 | 0·24 | 0·13 | 2·740 | 2200 | 4·545 |
| | a. | 0·30 | 0·40 | 0·30 | 0·27 | 0·23 | 0·16 | 0·07 | | | |
| Portland Cement | c. | 1·85 | 1·15 | 0·75 | 0·59 | 0·41 | 0·26 | 0·16 | 3·160 | 1650 | 6·666 |
| | a. | 0·15 | 0·35 | 0·25 | 0·21 | 0·19 | 0·14 | 0·04 | | | |

*Note:* c. = concentration after adsorption, gms./litre.
a. = quantity of bitumen (gms.) adsorbed per unit area (10,000 cm.²).

A second series of tests was carried out following exactly the same test procedure as previously described, with a view to determining the quantity of bitumen adsorbed by measuring the colour of the bitumen solution

" qualitatively " before and after adsorption. At this stage it would seem advisable to explain " chromatic index "—a term here used to express true colour.

Benzene was poured into the three glass troughs and the triode grid potential, set up as a result of the light falling on the photocell, measured on the potentiometer over complete spectrum range of the incident white light—that is, each of the filters violet, blue, blue-green, green, yellow-green, yellow, orange, red and infra-red was interposed in turn between the source of light and the glass troughs. The special " stop " referred to in the earlier test was cut out and the full beam of 1 cm. diameter directed on the cell. Table VI shows results of tests on benzene. The total of the mean in the last but one column, which is 3·2756, was termed 100

TABLE V.

| Concentration, in gms./litre after adsorption. | Bitumen Adsorbed, in grams per unit area of : | | | | | |
|---|---|---|---|---|---|---|
| | Penmaenmawr. | Delafilla. | Quartzite. | Mountsorrel. | Limestone. | Portland Cement. |
| 2·0 | — | — | — | — | — | — |
| 1·9 | — | — | — | — | — | — |
| 1·8 | — | — | — | — | — | 0·17 |
| 1·7 | — | — | — | — | 0·30 | 0·20 |
| 1·6 | — | — | — | — | 0·32 | 0·22 |
| 1·5 | — | — | — | 0·50 | 0·34 | 0·25 |
| 1·4 | — | — | 0·58 | 0·48 | 0·35 | 0·28 |
| 1·3 | — | 0·71 | 0·56 | 0·47 | 0·36 | 0·31 |
| 1·2 | 0·80 | 0·68 | 0·54 | 0·46 | 0·38 | 0·34 |
| 1·1 | 0·78 | 0·65 | 0·52 | 0·45 | 0·40 | 0·33 |
| 1·0 | 0·77 | 0·63 | 0·50 | 0·43 | 0·37 | 0·31 |
| 0·9 | 0·76 | 0·60 | 0·46 | 0·41 | 0·35 | 0·29 |
| 0·8 | 0·75 | 0·53 | 0·43 | 0·39 | 0·32 | 0·26 |
| 0·7 | 0·72 | 0·46 | 0·40 | 0·36 | 0·30 | 0·24 |
| 0·6 | 0·65 | 0·40 | 0·38 | 0·34 | 0·28 | 0·21 |
| 0·5 | 0·58 | 0·39 | 0·36 | 0·32 | 0·26 | 0·20 |
| 0·4 | 0·52 | 0·37 | 0·35 | 0·29 | 0·23 | 0·19 |
| 0·3 | 0·45 | 0·35 | 0·28 | 0·25 | 0·19 | 0·15 |
| 0·2 | 0·40 | 0·29 | 0·21 | 0·20 | 0·13 | 0·08 |
| 0·1 | 0·25 | 0·19 | 0·15 | 0·11 | 0·05 | 0·02 |

chromatic index. The seven different concentrations of Petmex bitumen in benzene were similarly tested and the total of the " mean " for each concentration, expressed as a percentage of 3·2756, gave the chromatic index for that particular concentration. Thus a 2·0-gram.-per-litre concentration had a chromatic index of 9·08 (Table VII).

To express these results graphically a very simple method was devised. Each of the separate colour values of a particular concentration was expressed as a percentage of the corresponding colour value of benzene. For example, 0·0155, which is the value for violet colour of 2-grams-per-litre concentration (Table VII), when expressed as a percentage of 1·2830 (Table VI), the corresponding colour value for benzene gave a figure of 1·21 per cent. This was termed " percentage transmission." These values, when plotted against their corresponding colours, show a true picture of the colour of a particular concentration (Fig. 4).

Two concentrations, 2 grams per litre and 1 gram per litre respectively, were tested for adsorption with Mountsorrel and Penmaenmawr aggregates. The "chromatic index" of the two solutions was determined in each case before and after adsorption, and the difference gave the idea of the comparative adsorptive capacity of the two aggregates.

TABLE VI.

*Benzene.*

| Colour. | Mean Wave-length, in milli-microns. | Transmission, in volts. | | | | Percent-age Trans-mission. |
|---|---|---|---|---|---|---|
| | | 1. | 2. | 3. | Mean. | |
| Violet . . . | 450 | 1·2830 | 1·2830 | 1·2831 | 1·2830 | 100 |
| Blue . . . | 465 | 0·4800 | 0·4800 | 0·4800 | 0·4800 | 100 |
| Blue-green . . | 490 | 0·5063 | 0·5077 | 0·5070 | 0·5070 | 100 |
| Green . . . | 520 | 0·6154 | 0·6169 | 0·6157 | 0·6160 | 100 |
| Yellow-green . | 555 | 0·1080 | 0·1080 | 0·1081 | 0·1080 | 100 |
| Yellow . . | 580 | 0·0500 | 0·0500 | 0·0500 | 0·0500 | 100 |
| Orange . . | 610 | 0·0427 | 0·0424 | 0·0430 | 0·0427 | 100 |
| Red . . . | 675 | 0·0045 | 0·0045 | 0·0045 | 0·0045 | 100 |
| Infra-red . . | 750 | 0·1849 | 0·1836 | 0·1847 | 0·1844 | 100 |
| Total . . | — | — | — | — | 3·2756 | — |

Chromatic Index 100.

TABLE VII.

*Panchrometer Analysis of Mexican Bitumen Petmex. Grade* 4.

Concentration—2·0 grams per litre.

| Colour. | Mean Wave-length, in milli-microns. | Transmission, in volts. | | | | Percent-age Trans-mission. |
|---|---|---|---|---|---|---|
| | | 1. | 2. | 3. | Mean. | |
| Violet . . . | 450 | 0·0153 | 0·0158 | 0·0154 | 0·0155 | 1·21 |
| Blue . . . | 465 | 0·0181 | 0·0182 | 0·0186 | 0·0183 | 3·82 |
| Blue-green . . | 490 | 0·0355 | 0·0355 | 0·0354 | 0·0355 | 7·10 |
| Green . . . | 520 | 0·0715 | 0·0715 | 0·0715 | 0·0715 | 11·60 |
| Yellow-green . | 555 | 0·0205 | 0·0204 | 0·0205 | 0·0205 | 19·00 |
| Yellow . . | 580 | 0·0120 | 0·0124 | 0·0125 | 0·0123 | 24·60 |
| Orange . . | 610 | 0·0143 | 0·0143 | 0·0143 | 0·0143 | 33·50 |
| Red . . . | 675 | 0·0026 | 0·0026 | 0·0026 | 0·0026 | 58·00 |
| Infra-red . . | 750 | 0·1160 | 0·1183 | 0·1194 | 0·1179 | 64·50 |
| Total . . | — | — | — | — | 0·3084 | — |

Chromatic Index 9·08.

## INFLUENCE OF THE STRUCTURE OF THE BITUMEN ON ADSORPTION.

To investigate the phenomenon of adsorption completely, it would seem advisable to separate the bitumen in its main constituent groups—namely asphaltenes, resins, oils—and to carry out adsorption experiments on each to find exactly which constituent is preferentially adsorbed. In this con-

nection, the separation of asphaltenes was carried out in accordance with I.P.T. test A.12. To separate resins and oils, the filtrate obtained from the above test was evaporated to 25 ml. distributed over 25 grams of fuller's

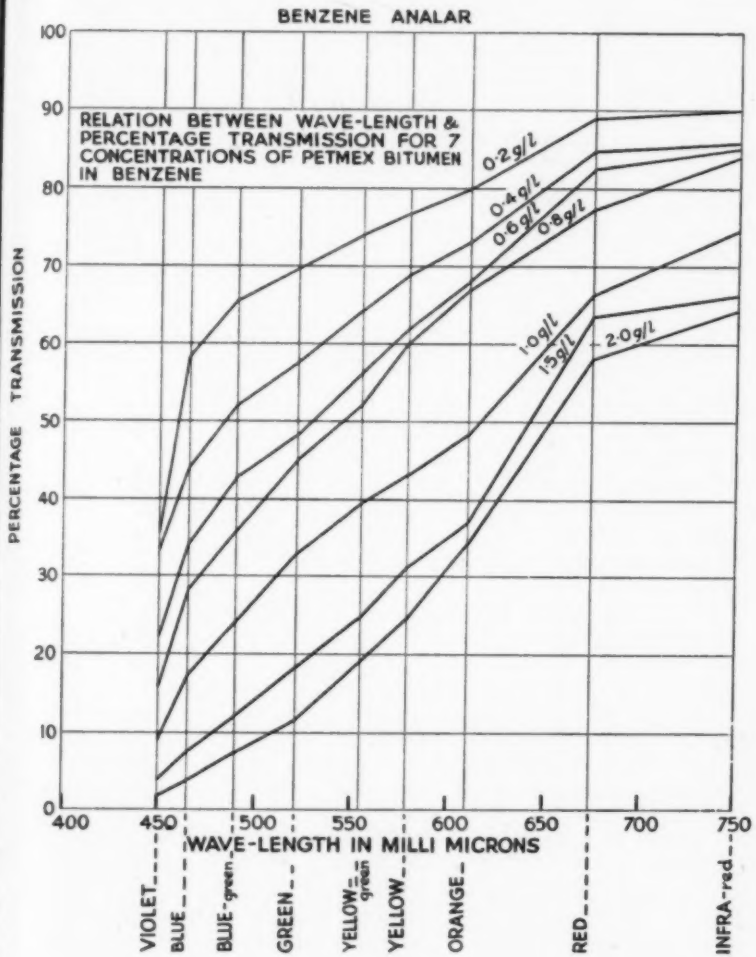


FIG. 4

earth and extracted hot in a Soxhlet with petroleum ether (boiling point 88°) in accordance with the recommendation of Professor Marcusson.[11] Resins adsorbed by fuller's earth were extracted with benzene, whilst oils dissolved in petroleum ether were separated afterwards by evaporating

the solvent. A check analysis was carried out similarly, and the results were as follows :—

*Petmex Bitumen. Grade* 4.

| | Asphaltenes, %. | Resins, %. | Oils, %. |
|---|---|---|---|
| First Analysis . . . | 26·32 | 27·08 | 46·60 |
| Check . . . . . | 26·35 | 27·00 | 46·65 |
| Mean . . . . . | 26·335 | 27·040 | 46·625 |

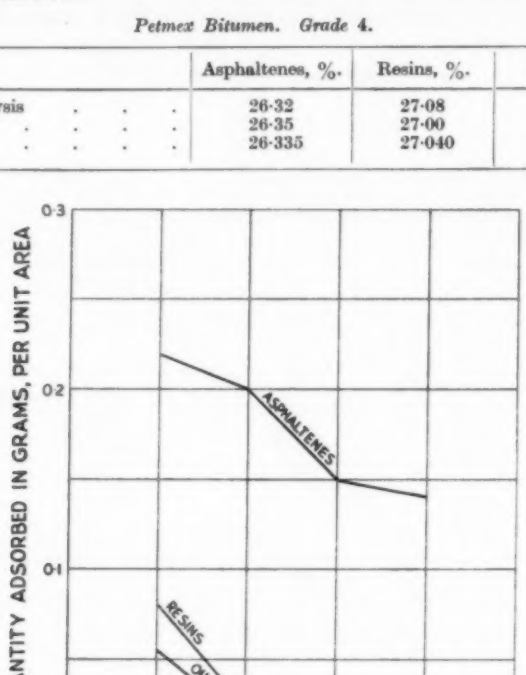


FIG. 5.
ADSORPTION OF MAIN CONSTITUENTS OF 'PETMEX' BITUMEN

Adsorption tests were carried out on these constituents separately, using one concentration of 0·6 gram. per litre in each case, and results obtained with four aggregates are shown in Fig. 5. A most significant point in the results was the stronger adsorption for asphaltenes in comparison with resins and oils. One likely explanation that seems to answer this preferential behaviour towards asphaltenes may be summarized as follows :—

" Asphaltenes consist of high molecular hydrocarbons of a predominantly aromatic character with comparatively low hydrogen content, formed by polymerization and dehydrogenation from lower molecular hydrocarbons."[12] It is a well-known fact that, according to the general principles of capillary chemistry, aromatic compounds are more strongly adsorbed than aliphatic, and hence the stronger adsorption of asphaltenes by aggregates.

In an attempt to find whether bitumens rich in asphaltene content would be more strongly adsorbed than those having a small percentage of asphaltenes, a Venezuelan bitumen, Mexphalte " E," with an asphaltene content of 16·90 per cent. was experimented upon. 2-grams-per-litre concentration of this bitumen was made and tested for adsorption with Penmaenmawr aggregate. The results were compared with those of Petmex with Penmaenmawr at the same concentration. It was found that Petmex was more strongly adsorbed than normal Mexphalte. Wilhelmi [2] carried out similar experiments on seven types of bitumens, and found that hard bitumens with a high asphaltene content were better adsorbed than soft bitumens, which generally contain less asphaltenes.

Having dealt with the structure of the bitumen, another important consideration would be to study the influence of the mineralogical and chemical composition of the aggregate on its adsorptive capacity. Davies and Messer,[16] who carried out some researches in this connection, found that there was no direct relationship between adsorptive capacity and chemical composition. In this paper the same result will be noticed in the case of Penmaenmawr and Mountsorrel aggregates. These aggregates are almost identical in their chemical and mineralogical composition, yet from Table V and Fig. 3 it will be found that Penmaenmawr has a much greater adsorptive capacity than Mountsorrel. In view of these observations, the following can be conveniently assumed to be a *possible* explanation for the greater adsorptive capacity of Penmaenmawr.

It seems that the smallest particles of Penmaenmawr aggregate may not be massive but possess a very fine microstructure, and that these particles are honeycombed with innumerable microscopic canals that bring about an enormous increase in the adsorptive surface. Therefore every time 7·522 grams of Penmaenmawr aggregate were taken to correspond to the arbitrary unit of surface area (10,000 cm.$^2$) during adsorption tests, actually this quantity presented a far greater adsorptive surface than calculated. This increase in the calculated surface area, which cannot be accurately estimated on account of lack of methods available, therefore accounts for the greater adsorptive capacity of the Penmaenmawr aggregate.

## The Practical Application of Adsorption Results.

It has not been found possible to establish by actual experimental results a direct relationship between adsorptive capacity of an aggregate and its influence on the design of bituminous mixtures for road construction, for the obvious reason that the design of the type of mixture involves several factors each requiring a thorough investigation. However, the application of the knowledge of adsorptive capacity of aggregates is discussed from practical considerations.

A bituminous mixture for road construction consists essentially of aggregate and " binder." The aggregate is used both in the form of larger aggregate and as a filler. It is a well-known fact that the addition of filler in suitable amount not only increases the inherent stability of the large aggregate, but also raises the efficiency of the bituminous cement as a stabilising agent by imparting a characteristic to the mixture commonly

accepted as toughness. This action of fillers has been partly attributed to adsorption by Popël.[13] Wilhelmi [14] has also proved that the stiffening action of fillers is very largely due to this adsorptive capacity. Further investigations were carried out by the same author [2] on the influence of adsorption on the mechanical properties of bituminous mixtures. Results of compressive strength and tensile strength as determined on mixtures made with slate, basalt, porphyry, calcspar, and quartz, and Mexphalte "E" bitumen, and adsorption isotherms for the same aggregates show that the values of the mechanical properties fall exactly in the same order as the adsorption isotherms.

In view of these results, it can be quite logically concluded that the efficiency of an aggregate as a stabilizing agent, and from the point of view of the mechanical properties of the bituminous mixture, can be estimated in the laboratory with a considerable degree of confidence by determining its adsorptive capacity. After all, the success of a bituminous mixture primarily and necessarily depends on the adherence between the aggregate and the bitumen. Adsorptive capacity is just a measure of the adherence.

## Conclusion.

The research undertaken and indicated in the foregoing dissertation has clearly brought out certain definite conclusions on the problem of the adsorption of bitumens by aggregates used for road-making purposes, and these may be set out as follows :—

(1) The determination of the adsorptive capacity of any road aggregate is an essential preliminary to its use, in view of the fact that the phenomenon of adsorption exercises a deep influence on the behaviour of bituminous pavements.

(2) Adsorption being fundamentally a surface phenomenon, the accurate determination of the surface areas of the aggregates is vital.

(3) An absolute and reliable order of adsorptive capacity can be established for road aggregates.

(4) Adsorption increases with the concentration of the bitumen solution to a limit of about 2 grams per litre.

(5) The assumption that adsorption is independent of the mineralogical and chemical composition of the aggregate is in part confirmed.

(6) The disperse phase of a bitumen (asphaltenes) is more strongly adsorbed than the dispersing medium (resins and inert oils)—that is, hard bitumens are more strongly adsorbed than the soft bitumens, which generally contain a small percentage of asphaltenes.

The technique adopted has established a method of assessing the value of an aggregate in terms of its power to adsorb a bituminous binder. The extended use of the principle and its expansion to cover all materials in regular use must lead to a marked advance in the construction of the asphalt road surfaces, and give a corresponding increase in their resistance to the destructive effects of traffic and weather.

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# ALCOHOL MOTOR FUELS*

By A. R. Ogston (Associate Member).

## Introduction.

The subject of the use of alcohol in motor fuel has always been a highly controversial one, especially when alcohol derived from agricultural sources is concerned, and few questions connected with the petroleum industry seem to have been responsible for greater divergences of opinion than the use of alcohol fuel for internal-combustion engines. Thus, on the one hand the majority of those connected with the petroleum industry are apt to regard the use of alcohol as uneconomic and altogether unnecessary, whilst it is also considered to be detrimental to engines, whereas, on the other hand, there is a certain section of opinion which maintains that alcohol is a very valuable, if not indispensable, constituent of fuel for high-efficiency engines, and succeeds in producing much data and evidence of tests in support of this view.

It is, perhaps, only natural that the petroleum industry should regard agricultural alcohol as a somewhat undesirable competitor, whilst it is understandable that interests connected with the manufacture of alcohol should be anxious to encourage any new outlets leading to increased consumption, and in this lie the origin of the two opposing points of view on the merits and demerits of alcohol fuel. However, in the present paper on the subject of the use of alcohol in motor fuels the author has endeavoured to keep an absolutely open mind and avoid bias in either direction. Perhaps it should be mentioned that although the author was closely associated formerly with the first two alcohol fuels to be marketed in this country, he is now no longer connected in any commercial way with the distribution of either straight gasoline or alcohol blends, and can genuinely claim to have no particular axe to grind.

## History.

The use of alcohol as a fuel for internal-combustion engines was first considered nearly forty years ago, when many experiments were made, mostly in Germany, to determine whether alcohol could be used in place of gasoline for the motor-car engines which were then being developed. It was evidently decided that the use of alcohol was not practicable in the engines of that epoch, which were mostly single-cylinder units with compression ratios of 3 or at the most 4 to 1, although it does appear to have been realized even then that if the compression ratio were increased to between 8 and 10 to 1, alcohol could be used as efficiently as petrol could in the low-pressure engines. Nevertheless, the use of power alcohol for motor cars did not become popular, no doubt on account of the difficulty of constructing in those days a reliable engine with a 10 to 1 compression ratio; moreover the price of petrol was extremely low, not being augmented, as it is to-day, by taxes amounting to 200 per cent. or so of its

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cost. Mixing alcohol with gasoline does not appear to have been considered to any extent, which was probably due to the fact that alcohol could not then be commercially produced with a water content of less than 5 or 6 per cent. : alcohol with a high water content is not miscible with gasoline.

The subject appears to have remained dormant until the advent of the Great War in 1914, when it was actively revived in Germany, who found herself facing a serious shortage of petroleum. Alcohol was, of course, in great demand for the manufacture of explosives and other war material, but it is fairly certain that the fuels used by the Germans for their aeroplanes and Zeppelins as well as ground transport consisted largely of mixtures of alcohol and benzole with whatever gasoline was available. Certain neutral countries also found themselves cut off to a large extent from supplies of petroleum, and in Sweden, for instance, almost the only fuel available during the War was a mixture of alcohol with benzole, acetone and turpentine; it appears that cars ran quite well on it, and that was long before motorists had started to become knock-conscious !

Since the Great War most countries have developed policies of economic nationalism, no doubt as a result of the tremendous difficulties which they experienced during 1914–18 in obtaining from overseas materials which they did not produce themselves. In those countries where no petroleum is found efforts have therefore not been lacking in searching for suitable substitute fuels which can be produced at home, and thus reduce or cut out altogether the imports of the foreign product. Legislation to enforce the use of alcohol as a motor fuel has accordingly been enacted in the following countries : Austria, Brazil, Czechoslovakia, France, Germany, Hungary, Italy, Jugoslavia, Latvia, Poland, Spain and Sweden. Incidentally, it is difficult to understand why Poland, which has a considerable indigenous production of petroleum, should have considered it necessary to enforce the use of alcohol in place of petroleum; presumably the agricultural industry must be regarded as more worthy of support than the Polish oil industry. Even in the United States, which has always so far had a surplus production of petroleum relative to its domestic requirements, there has been considerable agitation by the farming community for legislation to enforce the use of alcohol and gasoline mixtures, and such mixtures are now being marketed there in one or two districts, aided by tax exemption.

It is easy to realize that enforcing the use of alcohol, which may have to be purchased at an exorbitant price, has tended to antagonize the oil companies concerned as well as the motorist users, whilst in many of the countries which have just been mentioned there has been no opportunity for the oil companies' technologists to provide the most suitable mixtures, owing to the Government itself laying down the minimum percentage of alcohol—usually an excessive one—which it considers should be incorporated in motor fuel. It is significant to note, for instance, that in France alcohol motor fuels have gained such a bad reputation amongst motorists that in selling a straight gasoline an advertising feature is made of the fact that it does not contain any alcohol. On the other hand, in this country, where there has so far been no such legislation, many motorists are inclined to class alcohol as a luxury addition to their petrol.

The United Kingdom and Australia are, apparently, the only countries where alcohol motor fuels are being marketed without any Government compulsion, a situation which often mystifies those concerned with petroleum distribution in countries such as France, where the enforced purchases of alcohol which have to be made by the oil companies are considered very onerous. The adoption of alcohol mixtures by certain companies in Great Britain has, however, arisen through circumstances which are largely peculiar to this country. In the first place, the £1 per horse-power tax, based on cylinder bore only, resulted in the typical British car being powered by a small-capacity long-stroke engine of comparatively high compression ratio, which was much more prone to detonation than the power units of American or Continental cars. Consequently, until three or four years ago the British motorist was undoubtedly more "knock-conscious" than his counterpart in the United States, although it is doubtful whether this is still the case to-day, the Americans having recently been educated to appreciate anti-knock properties in gasoline as a result of the extensive advertising by companies distributing leaded fuels, whilst American motors to-day have very much higher compression ratios than they had formerly. The fact that a tax as high as eightpence per gallon was also levied on gasoline imported into Britain encouraged the use as a blending material of any home-produced product, such as benzole, which had the double advantage of being exempted from tax and improving the anti-knock properties of any ordinary gasoline which was mixed with it. Therefore, as soon as absolute alcohol became available at an economic price, it was only natural that companies which had not previously had the opportunity of marketing an anti-knock quality should be attracted to the possibilities of using alcohol to enable them to compete with the benzole mixtures and leaded fuels being supplied by their rivals.

The first concern to market an alcohol mixture to the motoring public in the United Kingdom was the Cities Service Oil Company, Ltd., which introduced their Koolmotor Blend in 1932. They were followed some two years later by the Cleveland Petroleum Products Company with "Cleveland Discol," which is now on sale throughout the greater part of the country.

## Manufacture of Alcohol.

There are, of course, several types of alcohols, which will be dealt with later on, but up till now ethyl alcohol has almost invariably been used for motor-fuel blending purposes, although methyl has been used to some extent in the preparation of special racing fuels; the former is often referred to as ethanol, whilst the term methanol is frequently used to designate methyl alcohol. The popularity of ethyl alcohol is no doubt largely due to the fact that it is the only type which has so far been produced on a very large scale, and is available at a price sufficiently low to render its use in motor fuel an attractive proposition. Actually, absolute ethyl alcohol has been available at this reasonably low price for a matter of only five or six years, and formerly supplies were of only 94 per cent. purity, their water content of 5 or 6 per cent. rendering admixture with gasoline impracticable except in very large proportions, where in order to obtain a stable mixture the alcohol content had to exceed 50 per cent. or so.

The dehydration of this alcohol was a slow and costly process until the discovery of a French concern, the Distilleries des Deux-Sevres, resulted in perfecting a method for removing the water content from 94 per cent. alcohol at a comparatively low cost; this process was quickly adopted by other distillers of industrial alcohol, with the result that absolute alcohol, which is miscible with gasoline in any proportions, became an easily obtainable commercial product, instead of a laboratory or pharmaceutical speciality.

Most of the ethyl alcohol produced in the United Kingdom is obtained by a process which utilizes black-strap molasses as the raw material. Molasses is the residual product obtained from cane-sugar refining, and is imported from tropical regions such as the West Indies, Java, Sumatra, Philippines, etc. Molasses is also obtained from sugar-beet refining but it is probably correct to state that practically none of the molasses obtained from our own domestic sugar-beet refining industry is used for alcohol production, the supply being reserved mainly for the production of yeast. Alcohol can also be produced from many other agricultural products which contain starch, such as corn and root crops, and in Germany large quantities are obtained from potatoes. Utilizing potatoes as the raw material is, however, very uneconomic, and to compete with other methods the process has to be heavily subsidized; this can be appreciated when it is realized that a ton of potatoes, to-day's market price of which can be taken at about £5, will produce approximately only 18 gallons of alcohol, so that on the basis of the price of the raw material alone the alcohol would cost about 5*s*. 6*d*. per gallon.

Alcohol can also be produced from maize, and one ton of this cereal, costing, say, £4 10*s*., will produce about 77 gallons, so that in this case the cost of the raw material would be equivalent to only 1*s*. 2*d*. per gallon. Where black-strap molasses is employed, the raw material cost per gallon of alcohol produced is still lower, and probably represents only 8*d*. or 9*d*. per gallon on present market values.

The figures just mentioned do not take into account the labour and capital charges entailed in the production of alcohol, and to cover these probably at least 2*d*. or 3*d*. per gallon would have to be added, as the process of manufacturing absolute ethyl alcohol is by no means as straightforward as distilling the gasoline off crude petroleum. On the other hand, it is of interest to note that the producers of industrial alcohol in this country obtain certain "methylating allowances" from the Government in respect of their output of power alcohol, in order to compensate them for the trouble and expense of denaturing the alcohol and rendering it undrinkable. Furthermore, the fact that various by-products are obtainable during the manufacture of alcohol, which would naturally tend to lower costs, has not been taken into account; for instance, considerable carbon dioxide is evolved during the fermentation process and some distilleries collect this and process it from the production of solid $CO_2$ for sale as "dry ice" for refrigeration purposes; this is possibly quite a profitable side-line.

The process of producing ethyl alcohol from molasses, which is the method at present used for the production of most of the industrial and power alcohol consumed in this country, consists briefly of causing rapid

fermentation of the molasses by the introduction of yeast cultures and maintaining the " wash," as it is called, at a suitable temperature. After two days the " wash " will have fully fermented, and will contain between 7 and 8 per cent. of alcohol, which is removed by distillation, the spent or residual liquor then being run off into the sewers or a river after suitable treatment and dilution with a large volume of water in order to render it inoffensive. By further distillation and condensation in fractionating columns, ethyl alcohol is obtained which is about 96 per cent. pure; the water content of 4 per cent. is then almost entirely removed by one of the special methods, such as the " Melle " process of the Distilleries des deux Sevres, the Merck process or the Drawinol-Merck system which was developed by the German Government. Other processes for effecting the final dehydration are the new I.G. German process which utilizes gypsum and a French process which has been developed in the United States which is based on the patents of M. Mariller and utilizes glycerine and ethylene glycol as the dehydrating agents.

Yet another dehydrating process which has come very much to the fore recently is one developed by a German concern—namely, the HIAG-Verein Holzkohlungs-Industrie of Frankfurt. Briefly, it consists of passing 95 per cent. alcohol through chambers filled with sodium acetate and potassium acetate in approximately equal portions—these salts have the unusual and very convenient property of absorbing only the water content, so that the alcohol emerges completely dehydrated. As soon as the salts have become saturated, they are easily regenerated by temporarily cutting off the flow of alcohol and passing superheated steam through at a very high temperature, whereupon the water is rapidly driven off. Unlike many dehydrating methods, the HIAG process has the virtue of extreme simplicity, but much credit is due to the research worker who found that the combination of those two metallic salts had such accommodating properties.

There are still a number of other sources from which alcohol can be obtained; ordinary wood or low-grade timber, for instance, can be converted into glucose by acid hydrolysis in accordance with the Scholler or Bergius processes, and subsequent refining of the glucose results in sugar and molasses, the latter, of course, being easily converted into ethyl alcohol. Various types of alcohol are also obtained by catalytic treatment of certain petroleum gases; thus, ethylene and propylene which are evolved in the cracking process are readily converted by suitable treatment into ethyl and *iso*propyl alcohols respectively. If alcohol is eventually adopted on a large scale for use in motor fuels, it is very likely that they will be produced from petroleum or coal-tar products rather than agricultural products.

The manufacture of ethyl alcohol in this country is very closely supervised by Government Excise officials. A duty equivalent to about £6 5*s*. per gallon is levied on any absolute alcohol used for potable purposes; alcohol used for power purposes is, however, free of any duty, but the Excise authorities naturally take every precaution to ensure that all the ethyl alcohol released for this purpose is genuinely consumed by engines, and not by human beings! Those who may not realize the extent of this supervision may be interested to know that the Excise officers often reside

at the distillery, and the valves on all the storage tanks and pipe-lines are actually locked, and can only be operated in their presence, and a detailed record is kept by these officers of all movements of stocks.

Power alcohol has to be rendered unfit for drinking purposes by a denaturing process which consists of adding a small percentage of pyridine and wood naphtha to it, but even when this has been done the alcohol is still kept under supervision, since it could still presumably be used for certain other purposes where it is subject to duty. Actually, power alcohol is released from the surveillance of the Excise authorities only when a minimum of 25 per cent. of hydrocarbons has been added to it. Therefore, a company distributing an alcohol blend must either arrange for 25 per cent. of benzole or gasoline to be mixed with the alcohol before it leaves the distillery, or, alternatively, it can arrange for its own blending depot to be bonded, in which case the straight denatured alcohol, or P.M.S.1 as it is termed (Power Methylated Spirit, stage 1), is despatched from the distillery in bonded rail tank cars or road wagons. The manhole covers of the latter have to be sealed after filling in the presence of an Excise officer, and on arrival of the tank car at its destination these seals must be inspected by another officer in order that he can verify that none of the alcohol has been withdrawn en route. The contents may then be discharged into a bonded storage tank, or, what will usually prove more convenient, the P.M.S.1 can immediately be converted into P.M.S.2—that is, mixed with 25 per cent. or more of hydrocarbons, after which the Excise officers lose all interest, provided the eightpence per gallon tax has been paid on any gasoline used for this purpose.

## Blending.

The blending of an alcohol fuel does not present any particular difficulties, the mixing being usually carried out in small storage tanks. For reasons which will be dealt with later on, it is very desirable that an alcohol blend being distributed for general sale to the public should also contain at least 10 per cent. of benzole. It is usual to mix the alcohol and benzole content first, which is then blended with the desired proportion of gasoline, and a typical blend would consist of 15 per cent. ethyl alcohol and 15 per cent. benzole with 70 per cent. gasoline. Satisfactory blending can be obtained by re-circulating, by means of a pump of suitable capacity, the contents of the blending tank, the capacity of which should not be too large. A 10,000-gallon blend can, for instance, be conveniently made up in a 30 ft. × 9 ft. storage tank equipped with an adjustable swing arm, so that, in re-circulating, the mixture can be drawn off by the pump from the bottom of the tank and discharged back again at or near the surface. It is preferable to fill the gasoline required for the blend into the tank first, which should then be carefully tested for the presence of water, either by means of water-finding paper or, better still, by drawing off a sample from the lowest part of the tank. Assuming that no water is detected, the alcohol and benzole may then be added. Once the blend has been made up, the most stringent precautions must be taken to guard against the ingress of any water at any stage of the distribution of the blend, for the accidental contamination by even 1 per cent. of water will cause the bulk

of the alcohol in a 15 per cent. blend to settle out from the gasoline. This is perhaps not so serious as it sounds, for actually in the case of a tank containing, say, 5000 gallons of alcohol fuel, 1 per cent. represents 50 gallons, and it is extremely unlikely that this volume of water would get into the tank by accident; on the other hand, the accidental ingress of just a few gallons of rain water into a tank containing 5000 gallons of blend would be of no serious consequence, for it would be completely absorbed in the fuel.

Perhaps it should be explained that water is miscible with alcohol in any proportions, but, water being almost completely immiscible with gasoline, the latter is only miscible with alcohol so long as the alcohol is practically water free. Consequently, if any appreciable quantity of water comes in contact with an alcohol blend, it immediately selects the alcohol with which to go into solution, which then becomes, as it were, insoluble in the gasoline content, and the mixture of alcohol and water settles out to the bottom of the tank. The addition of benzole increases the water tolerance of a mixture of alcohol and gasoline, which means that an alcohol/benzole/gasoline blend will tolerate a greater quantity of water before separation of the alcohol starts to take place. Nevertheless, even with blends containing as much benzole as alcohol, any contamination with water must always be rigorously guarded against, and every rail tank car or road wagon must be carefully inspected before use, the same applying to the underground storage tanks into which it is filled at garages.

With regard to the percentage of ethyl alcohol which should be used in a blend for sale to motorists, in the author's opinion this should be somewhere between 10 and 20. The calorific value of ethanol is only about 12,000 B.T.U. per lb., and it requires roughly one third less air for combustion than gasoline. Benzole, on the other hand, will support about 10 per cent. more air on combustion than is required by a similar volume of gasoline —volume because carburetter jets control the *volume* of fuel fed to an engine, and not the weight, and so, although 1 gramme of benzole has a lower calorific value than 1 gramme of gasoline, owing to the much higher specific gravity of benzole, 1 cubic centimetre contains approximately 10 per cent. more heat units than 1 c.c. of gasoline. Similarly, the gross heat value of 1 gallon of benzole is equivalent to about 153,000 B.T.U., which is about 14,000 B.T.U. higher than the heat value of a gallon of gasoline with a specific gravity of 0·730; the same quantity of ethyl alcohol would contain only about 100,000 B.T.U. Table I shows the respective amounts of air required by alcohol, benzole and gasoline for complete combustion.

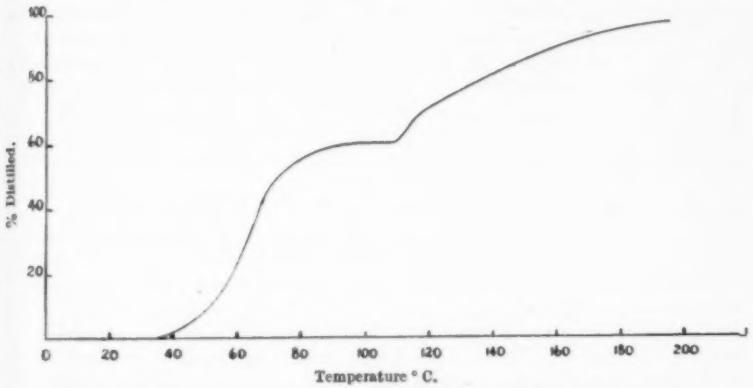
TABLE I.

*Air Required for Combustion.*

| | Lb. air/ lb. fuel. | Cu. ft. air/ lb. fuel. | Cu. ft. air/ gall. fuel. |
|---|---|---|---|
| Ethanol . . . | 9·2 | 114 | 906 |
| Benzole . . . | 13·3 | 164 | 1,443 |
| Gasoline . . . | 15·5 | 190 | 1,387 |

An alcohol blend which is to be retailed from service stations must suit the carburetter settings of the average car, and would stand little chance

of success if it were necessary to make adjustments before a car would run on it. Fortunately for the distributors of alcohol fuels, most carburetter settings are inclined to be a little on the rich side, and so, provided the alcohol content of the blend is kept below 20 per cent. and the lower calorific value is counterbalanced by a good proportion of benzole, satisfactory performance will be obtained without any modification of jet or choke settings. The author's own view is that such a blend should contain a percentage of benzole at least equal to that of the alcohol; thus quite a suitable make-up is 15 per cent. alcohol, 15 per cent. benzole and 70 per cent. gasoline. It is preferable to employ a grade of gasoline having as high a specific gravity, and therefore as high B.T.U. per gallon, as possible, without sacrificing volatility, which must be good, particularly at the lower end of the distillation curve if good starting and acceleration properties are to be




DISTILLATION CURVE OF A TYPICAL ETHANOL/BENZOLE/GASOLINE BLEND.

FIG. 1.

retained. This good front-end volatility is essential in order to offset the lower induction manifold temperature arising from the very high latent heat of vaporization of the alcohol and also its low vapour pressure; on the other hand, it must be borne in mind that the addition of ethyl alcohol to a volatile gasoline seems to increase the tendency for the latter to cause vapour lock troubles, so care must be taken to ensure that the front-end volatility is not overdone.

Fig. 1 shows the distillation curve of a typical blend of ethyl alcohol, benzole and gasoline.

Apart from the distillation and volatility characteristics of the gasoline used for alcohol blend, it is rather important to ensure that the gum content is not high, whilst the use of material having a high content of unsaturateds is also very undesirable. The addition of alcohol to any gasoline of which the gum content is on the high side, undoubtedly increases by a considerable extent the tendency for gummy deposits to occur in the induction manifold and on valve stems, and it would appear that ethyl alcohol in some way acts as a catalyst in assisting the deposition of gum, whilst the pyridine,

which must be used as a denaturant, probably aggravates matters. The author has actually experienced a case where a certain grade of cracked gasoline, which could be used straight without causing any gum troubles, when blended with alcohol deposited gum in the induction manifold at an extraordinary rate, deposits half an inch thick building up within a few weeks and rendering the cars in question unusable until the induction system and valves had been dismantled and the deposit scaled off.

### Corrosive and Solvent Effects.

Opponents of alcohol fuels frequently assert that one of the drawbacks is a tendency to cause corrosion of the fuel system, apart from their scouring action, which usually results in removing any loose rust or scale in the fuel tank, etc., the first time an alcohol fuel is used. Whether the charge of corrosiveness is justified or not depends largely on the type of metal used for the various parts of the fuel system. Zinc-coated or galvanized tanks and alloys containing a high proportion of zinc used for carburetters, etc., do appear to be slightly affected by alcohol fuels, a grey sediment usually accumulating continually in the float chamber and body of the fuel pump, if this too is of a similar metal, and unless this sediment is cleared out from time to time a stoppage may result. This sediment consists, mostly, of zinc oxide and zinc hydroxide, and is probably caused by some slight action on the zinc by the alcohol, and also by the small trace of water which is present in the 99·8 per cent. P.M.S.1 used for alcohol fuels.

In cases where dissimilar metals are used in a carburetter assembly, some slight corrosion of the more anodic metal may occur due to electrolytic action, and it seems possible that the alcohol may act as a conductor, whereas ordinary gasoline, on the other hand, is quite a good insulator. It is very difficult to protect these metal parts by means of a coating of lacquer, for whilst a lacquer can be made to withstand petrol and even benzole, it has so far not been found possible to make a lacquer which will resist a mixture of petrol, alcohol and benzole.

When alcohol blends were first introduced in this country four or five years ago, a good deal of trouble was encountered with cars equipped with certain types of fuel pumps. The design of one of these pumps fitted to a popular make of car incorporated a cork float which was coated with a synthetic resin lacquer, which, although unaffected by gasoline or benzole, tended to break down under the combined action of a third solvent, *i.e.* alcohol. The result was that the cork became, so to speak "water-logged," swelling up and losing its buoyancy, thus putting the pump out of action. Some difficulty was also experienced occasionally with the flexible diaphragms of fuel pumps due to the solvent properties of the alcohol dissolving out the proofing material with which the fabric of these diaphragms is usually impregnated. However, as the manufacturers of these components began to realize that they henceforward had to contend with the likelihood of alcohol fuels being used by motorists in general, designs were modified and improved materials obtained, so that to-day, so far as fuel pumps are concerned, it appears that no trouble need be anticipated where alcohol fuel is used.

The greatly increased solvent properties of an alcohol blend as compared with straight gasoline must, of course, be borne in mind during handling

and distribution. For instance, certain types of flexible hoses which may be quite satisfactory with petrol will be found to suffer rapid deterioration, due to the alcohol and benzole dissolving out the impregnating resin or varnish; specially resistant hoses must therefore be obtained. Incidentally, the most satisfactory material for this purpose is synthetic rubber, which rather surprisingly is far superior to any kind of natural rubber as regards its resistance to solvents. Alcohol blend may also be found to cause trouble with the packing material used for the glands of semi-rotary pumps, etc., but this difficulty can generally be overcome by careful adjustment and the use of special qualities of packing.

## Cylinder Wear.

Another criticism which has occasionally been levelled against alcohol fuels is that their use is liable to increase the rate of cylinder wear. If we accept the findings of certain investigators on cylinder wear to the effect that most wear is due to corrosion and occurs when the temperature of the cylinder walls is below 100° C., it can certainly be argued that more wear would occur with alcohol fuel, since the high latent heat of vaporization of alcohol must prolong to some extent the period which elapses after starting from cold until the temperature of the cylinder walls exceeds 100° C. So far as actual practice is concerned, the author's experience is somewhat conflicting; in one case where a fleet of vehicles, engaged on a type of service which involved much intermittent use of the engine, changed over from ordinary gasoline to alcohol blend, cylinder wear was found to increase from an average of 0·0005 inch per thousand miles to 0·0008 inch, representing an increase of 60 per cent. This means that assuming re-boring to be essential when 0·015 inch. cylinder wear has taken place, whereas formerly these vehicles ran for 30,000 miles, the use of alcohol blend reduced this mileage to under 19,000. On the other hand, the author himself has run a car for about 45,000 miles on alcohol blend and has not observed any abnormal rate of cylinder wear. It might be mentioned, however, that acting on the theory that the condensates from the products of combustion are liable to be corrosive, and therefore cause cylinder wear, apart from endeavouring to warm up as quickly as possible after starting, it has always been his habit to rev-up the engine immediately preparatory to stopping, and then to switch-off and close the throttle whilst the engine is turning over fairly fast, a procedure which the author believes ensures all traces of exhaust gases being completely expelled from the cylinders and helps to draw lubricating oil up round the upper part of the walls before the engine comes to rest. The author's favourable experience as regards cylinder wear may therefore be partly attributable to this practice, which he commends for what it is worth. Nevertheless, his impression is that cylinder wear is likely to occur at a somewhat higher rate using a fuel containing ethyl alcohol and benzole than would be the case with ordinary gasoline, particularly if the purpose for which the car or vehicle is used involves much intermittent use. It is also possible that the extra solvent properties of an alcohol/benzole/gasoline blend may tend to wash off the film of lubricating oil from the cylinder walls, especially during the warming-up stage when liquid particles of fuel are more numerous, whilst the fact that warming-up takes longer is also an adverse factor.

## Effect on Engine Efficiency.

It may be of interest now to consider some of the advantages and disadvantages of alcohol as regards its effect on engine performance. First and foremost of the desirable characteristics is its very high anti-knock value, which is attributable to two factors: first its high spontaneous ignition temperature as compared with gasoline, and secondly, its very high latent heat of vaporization. It is generally accepted that detonation in spark ignition engines is caused by the spontaneous ignition of a portion of the charge before the normal combustion flame started at the plug points has had time to reach the unburnt portion of the charge; in other words, the increase of pressure which begins as soon as the charge in the vicinity of the sparking plug is ignited, results in the temperature of the rest of the charge

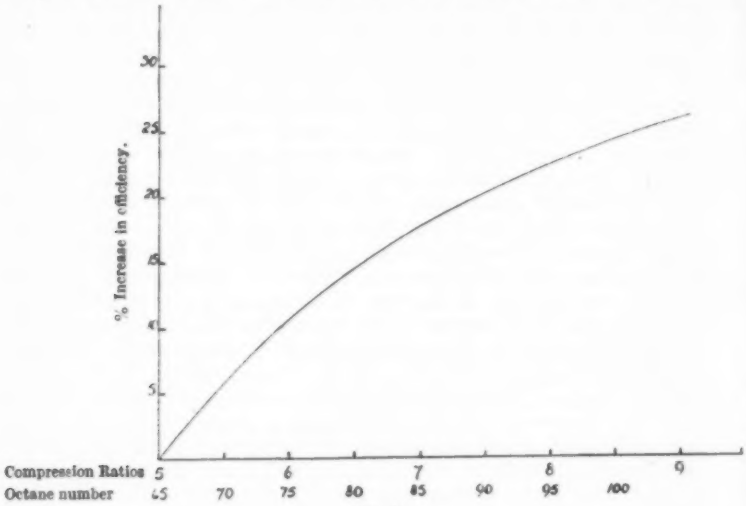



Fig. 2.

instantaneously rising to a point where spontaneous ignition occurs, in the same way as with a compression ignition or Diesel engine, except that in the case of the gasoline engine the whole of the fuel is already in the cylinder, and so the development of maximum pressure while the piston is probably still within a few degrees of top dead centre results in that sudden and audible shock to the cylinder head, piston, connecting-rod, etc., which we refer to as knocking or "pinking." It therefore follows that anything added to gasoline which will increase the temperature at which spontaneous ignition occurs will reduce the tendency for detonation to take place. It is obvious that the higher the compression ratio of an engine the nearer the charge approaches spontaneous ignition temperature as the piston reaches top dead centre. But alcohol, and especially methyl and ethyl alcohol, has a considerably greater latent heat of vaporization than gasoline, and so the temperature of the air/fuel mixture is appreciably

lower as it enters the cylinders and, of course, does not attain such a high temperature on compression.

It cannot be disputed that a blend of gasoline and ethyl alcohol is not as efficient a fuel as gasoline of a similar anti-knock value, on account of the relatively low calorific value of the alcohol. On the other hand, given a certain grade of gasoline of low octane rating, the addition of alcohol and benzole so as to raise its anti-knock value by ten or fifteen octane numbers will result in a fuel which will give more efficient operation in high-compression engines where the straight gasoline would have been handicapped by severe detonation. Fig. 2 shows an approximate relationship between engine efficiency and compression ratio, and along the scale of the

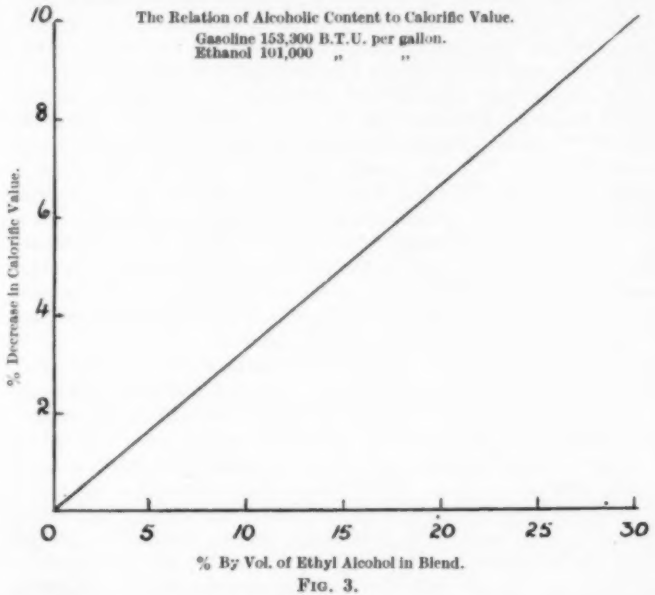



FIG. 3.

latter the minimum octane number necessary for efficient operation with the corresponding ratio is indicated, although no hard-and-fast rule can be used and these figures would vary considerably with different engines; the diagram is really only intended to make the principle clear.

It can, no doubt, be accepted that, at any rate with fuels of between 65 and 85 octane numbers, an increase of 1 octane number will permit an increase of about 1 per cent. engine efficiency, always provided that the engine has been properly designed to take full advantage of the higher anti-knock value. Now, although the alcohol response of different gasolines varies a good deal, as a general rule it can also be accepted that when ratings between 65 and 85 octane are being dealt with, the addition of 1 per cent. ethyl alcohol increases the knock rating of the gasoline by at least 0·7 octane number. Fig. 3 illustrates the percentage drop in calorific

value with increasing percentage additions of ethyl alcohol. Thus a 15 per cent. blend results in a loss of 5 per cent. calorific value, but the octane rating would have been increased by at least 10, which will accordingly permit an increase in efficiency of about 10 per cent., as was shown by the previous diagram. It is evident from this that alcohol, therefore, more than "pays its way," since its lower calorific value is offset by the higher efficiency which it is possible to obtain by better octane rating in the ratio of loss to gain of about 1 to 2. The inclusion of benzole, of course, still further improves the picture.

The author realizes that the foregoing conflicts with the arguments which are frequently put forward by those who view alcohol fuels with disfavour. For instance, in a paper which was written recently by two well-known American technologists,[1] it was claimed that any improvement in anti-knock and consequent efficiency provided by alcohol was more than offset by increased consumption due to the lower calorific value, and a table was given which appeared to prove this. A closer examination of this table, however, disclosed the fact that whilst it was stated that an addition of 15 per cent. alcohol gave an increase of 12 octane numbers, it purported to show that the possible increase of engine efficiency which could be obtained with this higher anti-knock value would be only 4½ per cent. This is obviously incorrect, and high anti-knock value would never command the premium which it does if such a relatively large increase in octane rating resulted in only such a small increase in efficiency. Furthermore, in the same table a 15 per cent. alcohol blend was shown to increase consumption by 7½ per cent., which figure is about 50 per cent. more than would be the case in actual practice.

Incidentally, there is one aspect in connection with the use of alcohol fuel about which the author feels quite convinced, and that is the tendency of the average motorist user to rate the performance of a well-proportioned alcohol blend rather higher than one would expect from a consideration of its anti-knock properties and other characteristics as determined by the usual methods of test. By this statement the author means to infer that if a lay motorist, running a sports type of car which is apt to detonate using ordinary gasoline, is persuaded to try an alcohol/benzole/gasoline blend of, say, 80 octane numbers (C.F.R. Motor Method), and then to compare it with, say, a leaded petrol of the same octane rating, in a large number of cases the motorist will assert that the alcohol fuel gives the better performance. The author is of the opinion that this is partly explained by the fact that the C.F.R. Motor Method of knock rating undoubtedly derates an alcohol blend by several octane numbers in relation to its performance in the average high-efficiency type of British car which usually runs with a fairly cool induction system. The C.F.R. Motor Method artificially heats the ingoing mixture to 300° F. before it reaches the cylinder, and the author thinks this must result in nullifying most of the effect of the high latent heat of vaporization of the alcohol fuel, which largely contributes towards its anti-knock properties. In this connection it may be of interest to mention that it has been reported that trials with ethyl alcohol blends in a modern type of air-cooled radial aero-engine resulted in pre-ignition,[2] although satisfactory results were obtained in high-compression water-cooled aero-engines.

It can, no doubt, be assumed that the intake and cylinder temperatures of the air-cooled engine would be appreciably higher than with the water-cooled job. This goes to confirm what has already been mentioned—namely, that the anti-knock properties of alcohol are largely derived from the relative coolness of the ingoing charge, and any large degree of pre-heating before the occurrence of combustion should be avoided, as otherwise an alcohol fuel loses much of its anti-detonating properties.

For the benefit, therefore, of those who may have been somewhat surprised at the degree of success obtained in this country by one or two brands of alcohol fuel within a comparatively short period of time, the author repeats that with many English sports type of cars the motorist will form the impression that his engine runs better on the alcohol mixture than it does on a gasoline which in the laboratory may have the same octane rating and be superior in the respect of calorific value. The almost fanatical preference that some motorists have for alcohol fuel may, therefore, not be so unreasonable, after all. It is certainly the author's experience that with certain types of high-compression engines an alcohol fuel does give a very smooth " feel " to the engine, and gives the driver the impression of better performance than when using a leaded gasoline of similar octane rating, although the fact is not disputed that if the acceleration and maximum speed are carefully verified by stop watch, it is quite likely that no difference will be disclosed in the respective performances of the two fuels.

In the case of engines of medium compression ratio, however, which will operate on ordinary gasoline without any detonation taking place, there can be no advantage at all in using a fuel of unnecessarily high anti-knock value such as an alcohol blend, for the motorist is, of course, unable to increase the compression ratio of his engine in order to take advantage of the higher octane rating.

This is a fact which is very often lost sight of by many motorists.

## The Higher Alcohols and Derivatives.

The author is of the opinion that future developments with the use of alcohol in motor and aviation fuels may embrace certain of the higher alcohols, in preference to the lower methyl and ethyl alcohols which alone have been used on any large scale up to the present. Alternatively, some of the alcohol derivatives, such as the ketones, may become popular as a means of producing fuels with exceptionally high anti-knock value for extra high-compression engines, and particularly aero-engines where the development of maximum power from an engine of given size and weight is far more essential than with engines operating on land. In this connection, it is interesting to note that the firm of Rolls-Royce, Ltd., have been experimenting recently with gasoline blended with certain of the ketones and, according to reports, have obtained some very encouraging results as regards freedom from detonation, power output and even low fuel consumption; the interesting and useful discovery has also been made that these blends have unusually good response to additions of tetra-ethyl lead.

Table II shows the principal properties of most of the lower and higher alcohols, together with some of the ketones, whilst for purposes of com-

parison the figures for gasoline and benzole are also included. It will be noticed that with the higher alcohols the calorific value is greater and tends to approach that of gasoline; on the other hand, that valuable property the latent heat of vaporization appears to become less the higher is the alcohol, which suggests that the anti-knock properties will also be found to be diminished. It has not been possible to obtain any information as to the spontaneous ignition temperatures of these higher alcohols, but assuming that they follow the same rule as in the case of petroleum, it would probably be found that the larger molecules have rather lower spontaneous ignition temperatures than the lower alcohols, in which case their anti-detonating properties would not be so good.

Of the higher alcohols, it appears that *iso*propyl would be one of the

TABLE II.

*The Properties of the Alcohols and Ketones.*

| Name. | Formula. | S.G. at 15·4° C. | Calorific Value B.T.U./lb. Gross. | Latent Heat Vapn. Cals./gm. | Boiling Point, ° C. | Solubility in $H_2O$ gms./ 100 c.c. @ 20° C. | Vapour Pressure mms./Hg. @ 20° C. |
|---|---|---|---|---|---|---|---|
| *Alcohols* | | | | | | | |
| Methyl | $CH_3OH$ | 0·793 | 9,330 | 267 | 64·7 | All proportions | 95·2 |
| Ethyl | $CH_3CH_2OH$ | 0·795 | 12,600 | 209 | 78·3 | ,, | 44·0 |
| *n*-Propyl | $CH_3CH_2CH_2OH$ | 0·805 | 14,930 | 169 | 97·2 | ,, | 14·5 |
| *iso*Propyl | $(CH_3)_2CHOH$ | 0·790 | 14,930 | 170 | 82·3 | ,, | 32·9 |
| *n*-Butyl | $CH_3(CH_2)_2CH_2OH$ | 0·810 | 16,140 | 141 | 117·7 | 8·3 | 4·7 |
| *iso*-Butyl | $(CH_3)_2CHCH_2OH$ | 0·806 | 16,140 | 138 | 108·1 | 9·8 | 8·8 |
| *tert.*-Butyl | $(CH_3)_3COH$ | 0·789 | 16,140 | 130 | 82·8 | All proportions | — |
| *sec.*-Butyl | $CH_3CH_2CHOHCH_3$ | 0·806 | 16,140 | 134 | 99·5 | 29·0 | — |
| *n*-Amyl | $C_5H_{11}OH$ | 0·817 | 16,960 | 120 | 140·0 | 2·7 | 2·8 |
| *tert.*-Amyl | $(CH_3)_2CH_2CH_2COH$ | 0·809 | 16,960 | 114 | 101·8 | Slight | — |
| *n*-Hexyl | $C_6H_{13}OH$ | 0·819 | 17,570 | — | 175·8 | 0·09 | — |
| *n*-Heptyl | $C_7H_{15}OH$ | 0·818 | 18,020 | — | 155·8 | Slight | — |
| *n*-Octyl | $C_8H_{17}OH$ | 0·827 | 18,370 | 97·5 | 194·0 | ,, | — |
| Benzyl | $C_6H_5CH_2OH$ | 1·05 | 14,760 | 111·6 | 205·8 | 4·0 | 0·1 |
| *cyclo*Hexanol | $(CH_2)_5CHOH$ | 0·962 | 16,600 | — | 161·0 | 3·6 | — |
| *Ketones* | | | | | | | |
| Acetone | $CH_3COCH_3$ | 0·791 | 12,200 | 155 | 56·5 | All proportions | 184·8 |
| Methyl ethyl ketone | $CH_3COC_2H_5$ | 0·805 | 14,870 | 106·0 | 79·6 | 22·6 | 77·5 |
| Diethyl ketone | $C_2H_5COC_2H_5$ | 0·814 | 15,900 | 90·8 | 101·7 | 5 | — |
| *cyclo*Hexanone | $(CH_2)_5CO$ | 0·945 | 15,500 | — | 155·0 | — | — |
| Gasoline | $C_nH$ 13·5 | 0·730 | 21,000 | 75·0 | 35·0/200·0 | Insol. | 90·0 |
| Benzole | $C_6H_6$ | 0·880 | 18,100 | 93·0 | 80·0 | Very slight | 74·3 |

most interesting from the fuel point of view. It has a calorific value about 20 per cent. higher than that of ethyl alcohol, and although the latent heat is about 20 per cent. less, it is still more than double that of gasoline. The volatility of *iso*propyl alcohol is reasonably good, the boiling point being, approximately, 82° Centigrade. Another point in favour of the use of some of these higher alcohols is that their response to additions of tetraethyl lead is believed to be better than is the case with methyl and ethyl alcohols, the lead response of which, according to reports, is rather disappointing. *iso*-Propyl has other advantages as compared with ethyl alcohol, not the least of which is the fact that it is free from the very many restrictions of the Excise Authorities, since it is not regarded as a potable product. As a matter of fact, *iso*propyl is sometimes used in the United States as a denaturant for ethyl alcohol, for, once mixed with the latter, it is practically impossible to separate it by distillation.[3] Although *iso*propyl is miscible with fresh water it is insoluble in salt water, and it is

therefore a comparatively simple matter to recover it from an aqueous mixture merely by adding sodium chloride. On the other hand, where any accidental contamination of water occurs with an ethyl alcohol/gasoline blend, it is usually impracticable to recover the pure alcohol.

*iso*Propyl alcohol can be manufactured in various ways, the two principal methods being : (1) the catalytic reduction of acetone and (2) the treatment of waste gases evolved in cracking petroleum. The latter process, which is undoubtedly the more economic, consists of scrubbing these gases with sulphuric acid, which converts the olefines into alkyl sulphuric esters, which on hydrolysis yield the crude alcohols, *iso*propyl alcohol being obtained by fractional distillation.

At present the higher alcohols are comparatively expensive, but no doubt if a large demand arose for *iso*propyl alcohol, for instance, so that it could be produced on a scale similar to that of the present production of ethyl alcohol, the cost would quickly come down, and there is no particular reason why it should be more expensive than the lower alcohol.

## Possibilities for Aircraft.

As a constituent of fuel for aero-engines, alcohol has certain advantages and also disadvantages. In certain circumstances, however, the former will probably outweigh the latter. The disadvantages are, of course, the lower calorific value of an alcohol mixture as compared with an equivalent weight of gasoline, for with aircraft the weight of the fuel is of vital importance, since it so directly affects the range and pay-load. Alcohol fuels have also been reported to cause trouble with the fuel system of some aeroplanes, due to the much greater solvent action, and any trouble of this nature is of course far more serious with an aircraft than with a land vehicle; nevertheless, it should be a relatively simple matter to provide flexible fuel lines, carburetter components, etc., which are unaffected. On the credit side, the anti-knock properties are the principal asset. Most high-duty aero-engines are supercharged nowadays, a practice which has its attendant problems, since increasing the pressure of the air/fuel mixture before it reaches the cylinders also increases its temperature, and thus renders it more prone to detonate; consequently, it is usual to have an intercooler to reduce the temperature of the " boost," as it is called, but this adds weight, and also sets up drag, since the radiating fins of the intercooler must be exposed in the air stream. If an alcohol fuel were used, its high latent heat of vaporization should very materially assist in reducing the amount of intercooling necessary between the supercharger and the induction manifold.

Another important advantage which should be provided by all the water-soluble alcohols is the fact that a fuel containing 5 or more per cent. will effectively prevent the formation of ice in the intake of the engine. Icing-up of the induction system of aeroplanes is liable to occur during certain weather conditions when the atmospheric temperature is within a few degrees of 32 Fahrenheit and when the humidity is high; it does not occur at extremely cold temperatures, and an aeroplane flying in the Arctic regions in winter would be quite immune, but the phenomenon is prevalent at times during the winter months in the British Isles and other damp

areas of similar latitude. It usually occurs when the machine is flying in cloud by means of its blind-flying instruments—that is, at a time when nothing could be less welcome than a gradual but rapidly increasing falling-off in power of the engine or engines due to the throttling effect of the accumulation of ice on the walls of the induction. To make matters worse, the trouble usually becomes more pronounced at full throttle, partly because many engines have provisions for reducing or cutting out all exhaust heating of the intake at the wide-open position of the throttle in order to improve volumetric efficiency and thereby obtain maximum b.h.p. Consequently, a pilot may be flying on two-thirds throttle, and noticing a fall in the engine revolutions will instinctively open up, only to make matters worse. Moreover, to add to the worries of the unfortunate pilot, it is more than likely that a certain amount of ice will also have formed on the wings, thus reducing their lifting efficiency, and whilst it is probable that the aeroplane would have maintained height with *full* engine power available, this is no longer possible when the engine as well is only functioning at 50 per cent. or less of its normal efficiency. It seems very probable that many of the bad crashes which have been occurring in Europe and America during the winter months, and the reasons for which are often unexplained, have been caused by icing trouble, and although alcohol does not, of course, offer any solution to the problem of ice formation on the wings and control surfaces, it does effectively prevent the engines icing-up, and it is therefore suggested that its possibilities in this direction should receive more attention than has been the case up till now. An alternative method is, of course, to provide sufficient heating of the induction to obviate the possibility of ice forming, but this will reduce the efficiency of the engine, and may even lead to detonation at a time when the maximum possible b.h.p. is required. Even if the use of a ready mixed alcohol blend is not approved for aircraft operation, the author suggests as an alternative that a relatively small tank be installed which can be used for containing neat alcohol and is inclined to consider this the better arrangement. This supply would be connected to an extra jet in the carburetter, which could be brought into operation at the will of the pilot and would be used whenever the atmospheric conditions were such as to denote the possibility of icing. In addition, the alcohol supply would be turned on during the take-off or whenever full power was required at low altitudes, in which case the anti-knock and cooling properties of the alcohol would permit the use of a much higher degree of "boost." The size of the jet could be proportioned so as to deliver between 10 and 25 per cent. alcohol in relation to the volume of gasoline being delivered by the main jets; some simultaneous adjustment of the air supply could be arranged. As a matter of fact, a carburetter on these lines has already been designed by the Claudel-Hobson firm.

Reverting to the detonation question, it appears that the situation in the aero-engine field is that in the very near future 100 octane fuels will have become a necessity for all high-efficiency engines. The methods envisaged at present for obtaining such a fuel involve the additions of blending materials such as pure *iso*-octane and *iso*propyl ether to a gasoline already containing the maximum permissible content of tetraethyl lead. It is obvious, therefore, that the supply of a suitable quality of

aviation fuel is becoming a much more difficult and complex problem than formerly. The blending agents to which reference has just been made are at present produced only in the United States, and their production is mainly restricted to countries with ample crude petroleum supplies, with their attendant refining facilities; bearing in mind the present policy of the American Government to prohibit the export of war materials, in the event of a war considerable difficulty might be experienced in obtaining these special hydrocarbons which would be essential constituents of the fuel required by our high performance fighters, bombers, etc. It is thought, therefore, that there is every justification for thoroughly investigating the possibilities of the use of the alcohols and some of their derivatives for aeronautical purposes, for in an emergency these could be produced in this country without having to depend on imported raw materials; for instance, some are producible from coke-oven gases, not to mention various other indigenous resources.

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# TRINIDAD BRANCH.

## FORESTRY IN RELATION TO THE PETROLEUM INDUSTRY.

By R. L. Brooks, Dipl.For. (Edin.).

*Summary.*

A paper on "Forestry in Relation to the Petroleum Industry," by Mr. R. L. Brooks, Dipl.For. (Edin.), Conservator of Forests, Trinidad, was presented to a meeting of the Trinidad Branch, held at the Apex Club, Fyzabad, on December 2nd, 1936. Commander H. V. Lavington, R.N., Branch Chairman, was in the Chair.

After dealing with the utility of forests in regard to their effects on climate, water conservation, and the prevention of erosion, Mr. Brooks dealt in detail with the problem of preserving the protective value of forests whilst at the same time permitting the exploitation of oil.

Recent applications for exploration licences covering the greater part of Trinidad, including most of the protective Forest Reserves other than those of the Northern Range, had produced a problem of major importance. This problem had, however, been satisfactorily solved by co-operation between the Lands Advisory Committee of the Government and the Petroleum Association of Trinidad. The latter body appointed a Sub-Committee to discuss the question and submit recommendations. This Sub-Committee, after instituting an inquiry to ascertain what proportion of forest need actually be felled for the intensive development of an oilfield in a Forest Reserve, was able to come to satisfactory agreement with the Lands Advisory Committee. Proposals were then drawn up concerning the total clearings allowed—a distinction being made between areas cleared once only and permanent clearings—and measures for preventing the concentration of these clearings in one area. The satisfactory solution of these problems provided an example of the importance of intelligent co-operation in achieving the best results in the interests of both Petroleum and Forestry.

The Paper was followed by an interesting Discussion in which the following took part:—Commander H. V. Lavington, Mr. J. W. Hardy, Mr. E. C. Scott, Lt.-Col. The Hon. H. C. B. Hickling, Mr. H. A. Bennett, and Mr. A. H. Richard.

(*The MS. of Mr. Brook's Paper may be consulted at the Institution by any member who is interested in the subject.*)

# THE MICROSCOPICAL EXAMINATION OF CRUDE PETROLEUM.*

By J. McConnell Sanders, F.I.C., F.C.S. (Member).

## PART I.—OBJECT, SCOPE AND METHODS OF INVESTIGATION.

SYNOPSIS.

The modern acceptance of the theory that petroleum owes its origin to the low temperature decomposition of organic matter has led the author to investigate the possibility of finding in crude oil, vestiges of those organized bodies which gave birth to it.

It was thought that, as in the case of coal, some portions of the primordial material might have been preserved, either because they were inherently resistant to decay, or because of the great preservative power of the petroleum itself, as evidenced by the results of recent investigations in other directions.

The object of the present paper is to give an account of the special apparatus and technique developed by the author for this type of investigation, and to record the results obtained by applying the method to a large number of crude oil samples, chiefly from Mexican and Roumanian fields.

The significance of the results and their bearing on problems related to the genesis of oil are discussed, as well as the possibility of utilizing the method for correlation purposes and increasing our knowledge of ancient forms of life.

In addition, some account is given of the chemical evidence which has supplemented the microscopical investigations carried out by the author.

### I. Introduction.

The value of the microscope in elucidating stratigraphic problems and for obtaining information about the past history and present constitution of natural deposits is too well known to require special emphasis.

To the oil geologist, sedimentary petrology and the intensive study of microscopic organisms both of fauna and flora are proving of increasing value and significance.

A study of the voluminous literature relating to the constitution of coal shows that microscopical evidence has played a very large and important part in building up our present wealth of knowledge concerning its constitution and mode of origin.

That such evidence is available depends on the fortunate circumstances that coal carries within itself, preserved throughout long periods of time, the visual evidences of its origin.

Stopes and Wheeler [1] define ordinary coal as a "compact, stratified mass of mummified plants which have in part suffered arrested decay to varying degrees of completeness."

These authors also sum up modern researches and the results of their own observations with the opinion that "not only the parts of plants most resistant to decay may be preserved entirely or almost unaltered but also any parts, however delicate, which were sufficiently early enclosed by the aseptic mass resulting from a particular type of breakdown of

* This paper is to be discussed at a meeting of the Institution in London on Tuesday, December 14th, 1937. Paper received August 17, 1936.

tissue in which bacterial activity is inhibited and which has special preservative properties."

Many attempts have been made to ascribe a common origin for coal and petroleum, and in accordance with the older theories of petroleum genesis, the incompatibility of geological and chemical evidence made the idea difficult to accept. Probably the issue was somewhat obscured by the then prevalent assumption that high-temperature conditions were a necessary factor in petroleum genesis.

With the modern acceptance of the theory that petroleum is born from organic material under low-temperature conditions, it seems possible to regard the two natural products, if not as brothers, at least as near cousins in relationship.

On the assumption that petroleum originated from the biochemical decomposition of organized material, it is logical to suppose that, as in the case of coal, some part of the primordial material would be either inherently resistant to decay or become enclosed at some stage in an aseptic medium which inhibited further decomposition.

Both classes of material, the decay-resistant and the decay-arrested, could presumably be discoverable in the mother-rock or source-bed, but also, with certain limitations, they could be carried by the oil itself to its final reservoir formation.

The limitations in question relate to the degree of free passage afforded to the suspended particles by the formations through which the oil had to pass during its migration.

When the path traversed by the oil was in the nature of a fracture, joint or solution channel in a formation such as limestone, there is little difficulty in visualizing a comparatively free passage for relatively large particles of suspended matter. In this connection, reference may be made to a paper by M. V. Howard and M. W. David [2] on "Development of Porosity in Limestones," and especially to the conclusion that continuous porosity may be developed mainly by solution by acids resulting from the bacterial decomposition of organic matter and by carbon dioxide formed during these processes.

In the case of an oil traversing or entering into a sand formation, the extent to which the latter may function as a filter is obviously determined by its texture, degree of compaction and particle size; but even in this case the passage of some amount of suspended matter is possible, as evidenced by actual data obtained and referred to later.

That crude petroleum has somewhat astonishing powers as a preservative medium receives substantial confirmation from the observations of Treibs,[3] who discovered chlorophyll porphyrins in twenty-two out of twenty-seven specimens of petroleum which he examined. He also found corresponding porphyrins in coal, oil-shale and asphalt, and in the case of an individual oil-shale was able to isolate the porphyrin and identify it as a compound with vanadium. The latter fact is of special significance in view of the known presence of vanadium in the ashes of petroleum, asphalt and some varieties of coal.

Equally significant is his observation that in petroleum and bituminous extracts a ferrous complex, apparently derived from mesoætioporphyrin, was present, which was characterized by complete stability to air.

Further evidence of the preservative power of petroleum is afforded by the discoveries of Ascheim,[4] who found estrogenic substances in peat, coal and petroleum, and together with Hohlweg prepared from these sources an oil containing a follicular hormone which was physiologically active.

It may be remarked that these hormones are not confined to the animal kingdom, but are found also in plants and in germinating grain; hence their occurrence in petroleum may indicate either an animal, a vegetable or mixed origin for oil.

Enough has been said to support the view that petroleum may have come down to us through the ages, not only carrying within itself the visual evidence of its previous contact with ancient forms of life, but also, in view of Professor Ascheim's discoveries, carrying vestiges of that life itself!

Based on this assumption, the author commenced a series of investigations, which have been extended over a number of years, and have included the examination of numerous samples of crude petroleum, representative of several geological ages, taken, with special precautions, direct from the wells in various producing areas, chiefly in Mexico and Roumania.

The object of the present paper is to place at the disposal of its readers some account of the methods of investigation followed by the author, and especially of the somewhat delicate technique which has been developed during the course of them. This is felt to be desirable because the subject appears to be capable of considerable expansion, and the studies should be carried into other fields which so far the author has not had the opportunity to enter.

The author takes this opportunity of acknowledging with gratitude his indebtedness to the many friends and colleagues who have assisted in the investigation, and especially to the Bataafsche Petroleum Maatschappij for permission to publish this paper, and to members of that Company's Geological staff for their suggestions, assistance and advice; also to the Field Managers and Staff in the oilfields of Mexico and Roumania, who have collaborated in the selection and procuring of samples, to Professor J. A. Mekel of Delft University for his kindly encouragement and advice, and to members of the chemical staff at the Central Laboratories of Shell Marketing Co., Ltd., who assisted in some of the chemical analyses.

Acknowledgment and thanks are also due to Dr. Helen Bancroft for her identification of the dipterocarpus wood referred to in Section VII, and to Miss M. E. J. Chandler for her identification of the silicified carex seed mentioned in the same section.

## II. Objects and Scope of the Investigations.

The information obtainable from the microscopical examination of crude petroleum may be of value:

(*a*) As an aid to elucidating the problem of its genesis.

(*b*) As a means for providing the palæontologist with a knowledge of those ancient forms of life, which were incapable of preservation by fossilization or petrification.

(*c*) As an aid to the solution of problems connected with the correlation of oils with reservoir formations or source deposits, and indirectly with questions of stratigraphical geology.

As a preliminary to the consideration of the above, it is necessary to have a clear idea as to the kind of material likely to be present in crude petroleum. At the outset it is clear that the subject should be regarded from a somewhat different viewpoint than that of the conventional palæontologist.

The conclusions of the latter depend largely on the assumption that the preserved or fossilized remains of ancient forms of life are contemporaneous with the sedimentary zones in which they are found.

With the realization that petroleum is capable of acting as a migratory embalming fluid, behaving, in fact, both as a preserver and carrier of the available evidence, the value of the latter for time-marking purposes is obviously diminished.

On the other hand, the organized remains embalmed in petroleum, not being dependent on any process of petrifaction, or anaërobic entombment, for their preservation, are not subject to profound chemical change in composition, or to physical change of shape by subsequent earth movements.

This means in effect that the soft-bodied and even delicately organized fauna and flora, hitherto unavailable to the palæontologist, may be looked for, and even expected to be present, and this considerably enlarges the scope of his researches.

As regards the type of organized material which may be looked for, reference has already been made to the limitations imposed by the conditions under which crude petroleum accumulates in its final reservoir. Hence, even if the significant material was originally of relatively large dimensions, it would probably present itself to the microscopist in the form of fragmentiæ.

This is not necessarily a disadvantage, since, to quote again Stopes and Wheeler: [5] "To an expert, whose eye is trained to deal with the minutiæ of fossil cells, a 'recognizable' piece of plant tissue may be a dozen cells of cuticle, or a wedge of wood so distorted by the twisting of the cell walls that the cell-lumina are almost obliterated; and we would go further, and maintain that to the real palæolobotanical specialist 'recognizable' plant remains need not even be whole cells. If the eye can be trained to recognize a small piece of wood, it may be trained to recognize a single wood tracheid, and if it can recognize a single tracheid, it may recognize a portion of the tracheid."

In dealing with the subject of petroleum genesis, the question whether one should look for macro or micro forms of life is still somewhat controversial. Dr. David White [6] recommends the co-operation of petroleum geologists, chemists and engineers in the micropalæontologic determination of the chemically organic micro-debris in ordinary accepted mother rocks. This would appear to connote a state of comminution for the organic matter before its conversion into petroleum.

The interesting and valuable work of Miss Taisia Stadnichenks [7] in this connection, using the micro-furnace, makes it appear that the organic remains in shale formation were chiefly in a state of incipient decomposition, and that what she terms an ulmic or humic colloidal binder had acted as the preservative aseptic medium for conserving the decay-arrested fragments of algal thalli, spore exines and similar matter.

There is considerable diversity of opinion regarding the actual mother-substance of petroleum. A summary of some recent opinions is given in the publication "Erdol Muttersubstanz," [8] which was reviewed by Trask [9] with some interesting comments, one of which is of special significance in connection with our present subject.

Referring to work done under the A.P.I. project for the examination of source-beds, Trask points out that although these indicate that cellulose is not a source of oil, because the quantity present is too small, yet, as shown by Brandt, the peridineans contain 40 per cent. of cellulose in their bodies, and with diatoms constitute two of the main groups of microscopic plants in the sea which have the ability of making organic matter from inorganic matter by the aid of sunlight.

They therefore constitute a basic source of organic matter in the sea, and underlying sediments derive their organic matter in part from their bodies.

Now, the dinoflagellates or peridineans are second only to the diatoms as food for both marine and fresh-water fauna. There are fresh-water, brackish water and open-sea forms, and the environment has a pronounced effect on them. Many thecate forms contain a colouring matter closely related to chlorophyll, and fat is often contained in the plasma. Their rate of multiplication is very great. M. V. Lebour [10] refers to work done at the Plymouth Marine Laboratory with a species of ceratium (one of the earliest known peridineans), showing that the rate of division for each cell would be about once every two days. Hence an enormous quantity of organic matter could be provided from this source.

Unlike the siliceous frustules of diatoms, the peridinean body is not provided with an inorganic component likely to be preserved as a fossil, although some of the other orders of the mastigophora class have chalky disks or carry silica in their membranes. The thecal armour of the dinoflagellates persists after death, however, and is capable of being preserved in crude petroleum. The author has found several fragments, very similar to the armature plates of a species of peridinean in oils from the cretaceous in Mexico, and while this may be taken as supporting evidence of Trask's suggestion, it has still to be explained how thecal cellulose can be transformed into hydrocarbons by natural low-temperature processes.

The classic researches of H. Potonié [11] are of interest in this connection. When dealing with the constitution of sapropel, Potonié describes and illustrates a varied assortment of organized material, both of fauna and flora, which he found preserved therein. Examples of all this material have been found by the author in crude petroleum in addition to other types, and he has also found in all sulphurous oils numerous examples of the minute spherical pyrite concretions which Potonié noticed.

A further point of interest is Potonié's allusion to resins, terpenes, balsams and the widely disseminated ethereal oils of the plant kingdom as co-operating in the formation of petroleum.

B. T. Brooks,[12] in supporting his plea for a low-temperature history for petroleum, refers to the same point, but stresses more particularly the existence of naturally formed hydrocarbons in nature, either as crystalline paraffins in the essential oils, or as normal heptane in two western pine trees and the prune-like fruit of a Philippine Island tree.

To complete the picture the vegetable waxes should be included, for many of them contain hydrocarbons. The leaves of the Javanese tree *Cera musæ* give a liquid hydrocarbon $C_{16}H_{34}$. While the latex of *Ficus ceriflua*, also from Java, contains a product intermediate between india-rubber and wax, which yields a liquid hydrocarbon, $C_{14}H_{26}$, by distillation.

An outstanding example of the natural production of hydrocarbons is provided by the Candelilla plant, *Euphorbia cerifera*, which grows profusely in the arid regions of Northern Mexico. This plant was found by the author [13] to coat itself with a hard brittle wax, amounting to from 4 to 6 per cent. of the dry weight of the plant. The wax contains from 40 to 50 per cent. by weight of the hydrocarbon hentriacontane, and the plant latex, when the plant grows under desert conditions, contains from 1 to 2 per cent. of indiarubber. Plants collected near the coast, or in regions of prevalent humidity, change their character entirely. They increase in size, lose nearly all their wax, and their latex is found to contain 43·5 per cent. of a resinous form of indiarubber.

It is noteworthy also that in the arid regions, the Guayule plant, *Parthenium argentatum*, grows profusely side by side with Candelilla, and in similar soil and climatic conditions secretes indiarubber in its tissues, but no wax.

There are many representatives of the Euphorbiaceæ family now growing in tropical regions, some of them large trees, 30 feet in height, and yielding either indiarubber or a product intermediate between indiarubber and resin.

The ability of these plants, and perhaps also of some ancestors of the same, to produce hydrocarbons, resins or caoutchouc apparently at will, in accordance with the exigencies of their environment, may be of significance, and in this connection it is of interest to record that the author has discovered the preserved remains of a tree in oil-well wax from Assam, together with fragments of fossilized wood from the same tree, derived from the genus dipterocarpus, and of which the resin was found dissolved in the wax and oil.

Remains of coniferous wood have been found in a number of waxy crude oils, and in some cases, but not in all, were accompanied by fragments of resin, still having apparently retained the shape of the cell in which they had been originally enclosed.

Diatoms as a source of oil have been the subject of considerable study, more especially in connection with Californian crudes, but accordng to G. M. Cunningham [14] it is an open question whether all the oil came from the miocene diatomaceous rocks. He alludes to the possibility of much oil originating in pliocene shales which are relatively free from diatoms. but in which the organic matter contains a jelly-like amorphous, flocculent material having imbedded decay-resistant vestiges of plant and animal remains.

L. A. Thayer [15] collected actual diatoms, extracted their oil-soluble content and analysed it. It yielded only 2 per cent. of hydrocarbons, but 52 per cent. of fatty matter and 43 per cent. of pigments. He then conducted experiments with a series of fatty acids, by decomposing them under anaërobic conditions, using special enrichment cultures in fresh and salt water. In all cases he obtained $CO_2$, $H_2S$, $CH_4$ and an inert gas.

He refers to the possibility of the pigments (which are largely of a hydrocarbon-like nature) being decomposable under anaërobic conditions also.

The author has found diatoms in many of the oils he has examined and also tests of radiolaria and sponge spicules, which, according to Gaylord and Hanna,[16] are also found in the mainly diatomaceous shales from the southern end of the San Joaquin valley, which they were attempting to correlate with the Monterrey shales. Hanna [17] refutes the widespread opinion that radiolaria in a sedimentary deposit indicate a profound depth of water during deposition. This is important in connection with our subject because the radiolarian remains found by the author have been in crude oils which carried evidence of being associated with deposits of shallow marine conditions close to the shore. Both diatoms and radiolarians were most frequently found in oils from miocene-producing formations, although cretaceous, jurassic and eocene oils furnished a few specimens.

With further reference to the type of organic or of organized material likely to be found in crude petroleum, reference should be made to the work of W. H. Bradley [18] and his microscopic study of oil shales, in which he shows that the most numerous identifiable remains are pelagic algæ mostly belonging to the cyanophyceæ and chlorophyceæ and filamentous fungi. He quotes some unpublished records by C. A. Davis which showed 112 distinct organisms including the following :—

| | |
|---|---|
| Phytoplankton . . . . . | 42 |
| Spores of fungi . . . . . | 30 |
| Filaments of fungi . . . . . | 29 |
| Pollen and spores of higher land plants . . | 28 |
| Uncertain organisms (cellular filaments) . . | 27 |
| Benthonic algæ . . . . . | 33 |
| Parts of higher plants . . . . . | 5 |
| Insects and fragments of . . . . | 3 |

He refers also to two fern annuli recorded by Davis, and to sclerenchymatous fibres and spiral tracheids found by himself, as well as a finely preserved water mite and the fragments of an anthropod leg found in Green River shale.

The above records are of great interest, in that they run closely parallel with the work of the author on crude petroleum, except that they appear to refer exclusively to the kind of material likely to compose the organic ooze of ancient lake-beds, and leave out of consideration the possible marine elements of oil source deposits.

The list of organisms considered by various authorities as being likely sources of petroleum could be considerably extended, but enough has been said to demonstrate that a microscopic study of the material actually carried by the oil is likely to be of considerable assistance in elucidating the matter.

Before leaving this part of the subject, mention should be made of an aspect of the matter which may naturally suggest itself to the mind of the reader.

If a sample of crude petroleum is found to contain a certain amount of preserved organic remains, how is one to know whether these were

derived from the reservoir rock and washed out of it by the oil, or originally brought into it by the oil from the primitive source-bed?

In most cases this question can be answered by examining cores or specimens of the reservoir formation, and this plan has been followed by the author in all cases where it was possible.

The case arises, of course, where oil and reservoir rock appear to have the same organisms in common. This may mean that the oil originated in the producing formation, and the evidence so obtained is of value.

But it may also mean that the oil did not acquire any such evidence until it reached the reservoir, or, alternatively, had its own preserved organic remains removed by filtration before it arrived.

This difficulty is met by careful consideration of the type of organism found. It may be possible to decide that certain organic remains could not have been preserved in the reservoir formation, and therefore must have been preserved and carried by the oil. In many cases observed by the author the material was found in a state of partial but arrested decomposition, which pointed to the oil as the most likely arresting and preservative medium.

But even in the ultimate event that uncertainty exists, the microscopical evidence may be of value for correlative purposes, especially where a number of wells are under observation. Water infiltration with the possibility of finding and recognizing its contained micro-organisms is also a factor not to be disregarded.

As an indication of the kind of material likely to be present, and therefore worthy of further research, a list is given in Part II, with drawings and photographs of some of the organized material actually found in crude petroleums, from various sources, together with comments arising from the author's own observations.

## III. Chemical Evidence as an Aid to Microscopical Investigations.

In the course of his examination of the organized material found in crude petroleum, the microscopist will naturally resort to a multitude of micro-chemical methods in order to assist him in the identification of certain classes of matter or differentiate between tissues or other structural elements. It is not proposed to deal here with such methods, since they are well known, or can be found fully described in standard publications.

Apart from this, the author has found it to be of great assistance to supplement the microscopical investigations with chemical tests on the oil itself, or on its ashes.

Certain metallic elements, notably nickel, vanadium, lead, iron and in a lesser degree copper, manganese, gold, molybdenum, magnesium and aluminium, are known to exist in crude petroleum, apparently in some form of organic combination. Hence, if an oil is found to contain such elements, it is a logical sequence to look for any organisms from which it could possibly be derived.

Alternatively, if organisms are found which are known to secrete, absorb, or inherently contain such elements, valuable corroborative evidence of the part played by the organism in its association with the oil may be obtained by an analysis of the latter.

In all cases it should be understood that in the case of metallic elements, only those which exist in the oil in a state of organic combination have any significance. Oils as they come from the well are liable to contain very finely divided mineral matter in suspension, sometimes held up by emulsification with water. Hence, an analysis of the oil should be carried out only with the perfectly dry sample, which has been filtered through a medium fine enough in texture to hold back the finest particles. The author has used unglazed porcelain or sintered glass for this purpose.

### *Vanadium and Nickel.*

The association of vanadium with chlorophyll-porphyrins has already been mentioned, but the metal is also found in the blood of the Tunicata, which probably accounts for the varied colour of these animals.

Vanadium is also found in Holothurians and sea-urchins, and in the ashes of some marine plants.

Hence, if a crude petroleum is known to contain vanadium, it is of interest to examine it for the remains of such flora and fauna which might have contained the metal in a state of organic combination.

In the case of marine fauna it may be observed that if the animal has been subjected to gradually increasing unfavourable conditions, such as would be preliminary to its death and inclusion in a sedimentary oil-forming deposit, it may have become de-differentiated before such inclusion, and be found in the oil only in a very simple form. The gradual dilution of salt by fresh water carrying terrestrial debris might provide such conditions.

Nickel is often associated with vanadium in the ash of crude petroleum, but this is not invariable. The author has found oils with nickel but no vanadium, and vice versa.

Information relating to the distribution of the metal in the animal and vegetable kingdoms is somewhat scanty. According to G. Bertrand and M. Macheboef,[19] it occurs with cobalt in all organs of mammals except muscular or fatty tissues.

Especially high is the nickel content of the human liver, the pancreas of the bull, the feathers of birds and the flesh of molluscs.

Bertrand and Mokragnatz [20] found nickel in twenty-three vegetables, varying from 0·01 mgm. in the tomato, to 2·00 mgms. in the pea, per kilogram of fresh material. The same authors [21] found 0·00136 per cent. and 0·00174 per cent. of nickel respectively in two samples of arable soil.

The occurrence of nickel in insects does not appear to have received much attention. E. B. Vvarov [22] found 0·009 per cent. in the ash of the locust, as well as copper, iron, manganese and other metals.

P. Rona, J. A. Parfentjev and H. Lippman [23] analysed the ashes of a number of insects in order to investigate the action of the metals present in accelerating the oxidation of cystine.

They found that copper and iron accelerated oxidation, but after the removal of these metals the residue still acted as an accelerator, which fact they attributed to the presence of lead and other metals. In the author's opinion it is quite likely that nickel was responsible for the effect.

The high nickel content of birds' feathers suggests that, like the copper content of turacin in the quill feathers of the plantain-eating Touracous,

the metal may be associated with the melanin or lipochrome pigments. On the other hand, it may play a functional part in the oxidation of cystine, and thus be a necessary component of the process of rapid metabolism in birds.

It would appear to be of interest to examine more closely the possible presence of nickel in the insect organism, in view of its apparent association with insect remains in oils of high nickel content.

It is worth recording that in the oils containing nickel examined by the author, fourteen out of thirty-five Mexican samples carried insect scales, and three the barbules of birds' feathers. Three oils which contained nickel but no vanadium were particularly rich in diatoms and insect remains; they came from a miocene formation.

With one exception, the highest nickel content was carried by an oil coming from the cretaceous in Mexico, and this oil carried insect remains and feather barbules as well as diatoms.

The possible relation of nickel to diatoms is also of interest. All the Mexican oils examined by the author which contained diatoms, also contained nickel. A number of Roumanian oils contained nickel, and either diatoms or remains of molluscs, which feed on diatoms.

It is recorded by W. B. Shirey [24] that the coke from Californian crude derived from San Joaquin Valley contained 4·35 per cent. of nickel in its ash. This crude is closely associated with a diatomaceous source.

The fact that diatoms are food material for the vanadium-containing ascidians suggests a possible reason for both vanadium and nickel to be found together in certain crude oils.

The frequency with which genera of the *Chætoceræ*, such as *Bacteriastrum* and *Rhizosolenia*, are found in the stomachs of ascidians, salpæ and holothuriæ, suggests that these animals have a predilection for these awn-embellished diatoms; hence their presence in oils which contain vanadium would be highly suggestive.

### *Phosphorus.*

On the assumption that proteins in the primitive source material of petroleum might be evidenced by the presence of phosphorus in the oil, the author had a number of crudes examined for that element. Out of thirty samples, comprising three miocene, two oligocene, three eocene, twenty-one cretaceous and one of jurassic derivation, thirteen contained traces of phosphorus, and of these eleven came from the cretaceous and two from eocene formations.

There was nothing discoverable by microscopical examination to account for the presence of phosphorus, and in the case of two cretaceous oils from the same field, one contained the element, but not the other.

### *The Halogens.*

Iodine and bromine are known to form organically combined compounds in the animal kingdom, instances being dibromindigo found by Friedlander in Tyrian purple, secreted by the glands of *Murex brandaris*, and an iodine compound, discovered by Bauman in the thyroid gland. Organically combined chlorine compounds have not so far been found in

animals, but Nolan, and independently Koller and St. Pfau, have isolated a number of chlorine compounds in certain lichens.

Now, fragments of lichens and their spores occur quite often in petroleum, and it was thought to be of interest to look for chlorine in the oil. Out of fifty-nine samples tested, traces of the element were found in twelve, but definitely identifiable remains of lichens were not found also in all those containing chlorine.

*Other Inorganic Elements.*

The association of magnesium with chlorophyll, and of aluminium with certain plant tissues (especially the *Lycopodiaceæ*), should not be lost sight of, and these metals are frequently found in the ashes of crude petroleum, as well as iron.

Manganese was the subject of a special search by the author, but has not so far been found in crude oils.

The possible relation of lead, molybdenum, copper and gold to any organism likely to have contributed to the formation of petroleum is very obscure in our present state of knowledge.

*Organic Components.*

In association with the microscopical work, the organic constitutents of crude petroleum other than the hydrocarbons which make up its main bulk may be of great importance. This comes about because the recognition of certain organized bodies in the oil may lead the microscopist to discover that substances normally present, or expected to be present in the living organism, are absent from it in the preserved state. If subsequently found dissolved in the oil, such substances afford confirmatory evidence of the association of the oil at some stage of its history with the organism in question.

*Resins, Pigments and Essential Oils.*

The resinous components of crude petroleum, although probably very minor constituents in the majority of cases, are deserving of more attenton than has hitherto been accorded to them.

The tendency of certain oils to form emulsions with great facility, the property possessed by certain asphaltic residuals to form gels when cut back with light distillates, and the increase in viscosity on storage shown by certain fuel oils, are quite possibly due to, or influenced by, the presence of resins.

The author has frequently found the probable source of such resins in crude oils which he has examined microscopically. Sometimes the resin itself has been found, showing that it was insoluble or only slightly soluble in the oil, and, as in the case of many fossil resins known to the paint and varnish industry, the operation of distillation provides just that preliminary heat treatment which results in the solubilization of the resin, which then appears dissolved in the still residues.

In some cases, where a resin is soluble in petroleum without heat treatment, the microscopist will only find its probable source, not the resin itself. Spore-coats and cuticles or resin cells in fragments of wood may be significant in this connection.

The variation in the fluorescence colours of crude petroleum when irradiated with ultra-violet light may be due to resins or specific pigments, and the toxic action on the human skin occasionally noticed may be due to euphorbiaceous resins, some of which are known to have this effect.

There are many references in the literature relating to the presence of resins in coal, and many of the conclusions arrived at regarding its presence in the latter are also applicable to petroleum.

In the author's experience the presence of resins and essential oils in certain crude oils is often betrayed by characteristic odours, when the masking effect of hydrogen sulphide has been removed. The turpentine-like smell of oil carrying vestiges of coniferous wood, the peculiar and very characteristic odour of the euphorbiaceous latex resins, the smell of gutta-percha and caoutchouc, of carvone and eugenol, have occasionally been noticed; but so far attempts to detect recognizable remains of the plants producing such substances have met with only moderate success.

The inclusion of pigments in crude oils is also worthy of further study, and in certain cases would appear to be characteristic of definite source origins for the oil. Mention may be made here of a case where the red colour of an Eastern crude was traceable to the colouring matter of kamala (*Mallotus philippinensis*) or some ancestor of the same, remains of which were found in the oil. It is possible that the spectroscope could be usefully employed in the study of the natural colours of crude petroleums.

### *Asphaltenes.*

The material precipitated from crude oil by ethyl ether or light petroleum spirit may be referred to here, since occasionally it may be of great interest in conjunction with the microscopical investigations. The following examples from the author's observations will demonstrate this :—

The asphaltenes in the large number of Mexican cretaceous crude oils were all found to contain vanadium and sulphur, and usually, but not invariably, nickel as well.

They did not, however, contain as a general rule the whole of these metals originally present in the crude, but for oils of a certain geological age, the vanadium and sulphur content tended to be constant.

There was apparently a close association of the asphaltic component with vanadium, since the latter could not be removed from solutions of the asphaltenes by dilute mineral acids or alkalis.

The inference was that there were two kinds of vanadium complex present, one intimately associated with the asphaltenes, the other not precipitated by (*i.e.*, soluble in) the precipitant. One may have been a chlorophyll-porphyrin compound, the other of marine animal derivation.

Now, under the microscope these oils were found to contain abundant evidence of both marine and terrestrial flora and fauna.

An oil from the presumed source formation in the jurassic differed from all the cretaceous oils in having no vanadium associated with its asphaltene content, although both it and nickel were present in the crude.

Moreover, this source oil was of lower specific gravity and sulphur content, and richer in low-boiling-point hydrocarbons than the cretaceous oils.

Microscopical examination of this oil, and of a core taken close to the

producing horizon, showed the prevalent organisms to be terrestrial rather than marine.

The evidence of the combined chemical and microscopical examination leads to the inference that the primordial oil had increased its asphaltene and sulphur content, and received an increment in vanadium and nickel, during its migration from the source formation, for neither concentration by loss of light fractions nor any internal change in the oil would account for the difference in general character between it and the cretaceous oils.

The simplest explanation appeared to be that the cretaceous oils were derived from more than one source, not only from the jurassic, and this fits in every well with the fact that the cretaceous oils differed amongst themselves very considerably in their wax content.

Similar correlations between the chemical and microscopical characters of crude petroleum will suggest themselves to other investigators, and the eventual utility of such observations will increase as more data become available.

## IV. Methods of Investigation.

### (a) *Samples.*

In order to obtain results of practical value, it is an indispensable condition that samples for microscopical investigation should be as free as possible from adventitious matter. Samples taken from storage tanks or containers exposed to contamination by dust are useless.

Wherever possible, samples should be taken from the flow-line of a well, or bailed directly from the tubing, and immediately placed in clean and dry receptacles, which must then be hermetically sealed.

It is also desirable that the microscopist has available the fullest information relative to the samples and sampling conditions. Special forms, to be filled in by the sampler, and despatched with the sample, are very useful in this connection. Items to be included should comprise the exact location of the well, the nature of the producing formation, the depth of the formation and total depth of the well. Under the heading "Conditions of sampling" it should be stated whether the oil was obtained from the well when flowing or on the pump, by bailing, swabbing or by skimming from the surface of entering water. If the sample is from an oil-show at a specific depth, the latter should be given, and to aid in tracing the sample after despatch, it is desirable to describe the container, the quantity of oil it contains and its labelled serial number or other distinguishing marks, as well as the route by which it is sent. If the oil from the well is emulsified with water, it is better to despatch it to the laboratory in that condition rather than attempt to dehydrate it on the field.

As regards the amount of sample to be taken, it is always desirable to have a quantity sufficient to "dilute" the effect of accidental contamination. The amount required for the microscopical examination is not large—from 100 to 250 ml. is usually sufficient—but this may be taken from 5 gallons of the original, well-mixed, sample.

Even under the best conditions the entry of adventitious matter is difficult to prevent entirely, but with practice and experience with a large

number of specimens, the operator learns to distinguish between material which has dropped recently into the oil and that which has been immersed in it for long periods of time.

Additional to the information relating to the sampling conditions, it is frequently useful to have available the history of the well and the usual drilling log.

Core samples from the well can also be examined by a modification of the method used for oil, and are taken with due precautions to avoid contamination until they reach the laboratory.

(b) *General Outline of the Method.*

Each sample is treated as a separate problem, and only by experience will it be learnt how best to modify the procedure in order to secure the most useful results. In general terms, however, the oil is first diluted to an extent determined by its consistence with a suitable solvent. In the majority of cases, water-white kerosine, carefully filtered before use, can be used, and is the most economical diluent when a large number of samples are to be examined.

With heavy viscous, asphaltic oils, benzol or carbon-bisulphide may be required.

At this stage any water present in the oil may separate, and should be drawn off with a separating funnel, care being taken not to draw off the material which frequently collects at the interface between the aqueous and oil phases. It is highly desirable that the diluted oil should be free from water, but a drying agent should not be used.

The diluted oil is next strained through a small brass sieve for the purpose of removing any contaminating substances such as cotton-waste fibre, which is very frequently present. If previously moistened with kerosine, the sieve also serves to hold back any globules of water still held by the oil. The size of sieve mesh is a matter for careful consideration, and should never be fine enough to retain micro objects which are to be the subject of final examination. Its primary object is to remove extraneous, *i.e.*, recent, material; but it may happen that objects of interest in the investigation are large enough to be held back by a fine mesh, or may be entangled in the foreign matter, and hence retained with the latter.

Experience has shown that the micro objects carried by the oil rarely exceed 100 microns in their largest dimension, and the majority are much smaller. Consequently a No. 80 U.S. Standard sieve, which has a sieve opening of 177 microns, is not too fine, and will hold back most, if not all, of the foreign material. In any case, after the screening operation the surface of the sieve should be washed with kerosine, benzol or carbon-bisulphide to remove oil and asphaltic matter, and examined carefully with a hand lens. If any object of interest appears to be present, the last traces of solvent should be removed by drying in a current of warm air, and the sieve, with its contents, immersed in distilled water for subsequent treatment.

The sieve should be preferably of small size, those used by the author being in the form of conical cups, turned from brass, and polished inside, the bottom being 1 inch in diameter and the junction between wire mesh

and frame filled smoothly with solder, so as to leave no lodgment for particles, and provide for easy cleaning.

The next and subsequent stages of the operation consist in the gradual concentration of the micro objects by means of special filters, combined where necessary with special methods of separation by gravity, or centrifugal action.

In order to segregate the objects without injury, it is important to realize that some of them may be of very soft and delicate nature, and others brittle and fragile, and that there will always be present simultaneously a much larger proportion of comparatively unimportant mineral matter, such as iron rust, well scourings, sand, limestone, etc. During the process of isolating the organized remains it is important, therefore, to avoid anything in the nature of mechanical trituration or friction between the particles, which would destroy distinguishing features or separate component parts of micro-organisms.

The first concentration is performed by the use of a water-soluble, oil-insoluble filter mass, which when eventually dissolved in water to release the entangled micro objects, results in a solution chemically inert towards the objects, and of a suitable density to ensure a partial separation of the light from the heavy particles.

Of a large number of substances tried for this purpose, the author has found the most satisfactory material to be the tough, fibrous crystals of sublimed ammonium chloride, the sal ammoniac of commerce, but in a high state of purity. The preparation and manipulation of this soluble filter will be described in the next section.

After filtering the diluted oil through the soluble filter mass, the latter is washed successively with various organic solvents so as to remove all oil and bituminous matter, the final solvent removed by warm air, and the entire filter dissolved in distilled water. The solution nearly saturated with the salt has a density sufficiently low to allow the greater part of the mineral matter to settle out, leaving the organic objects floating or in semi-suspension.

Some fossilized organized material and siliceous or calcified objects may separate together with the mineral matter, so that the heavy and light objects in the sal ammoniac suspension are separated in a specially designed micro-separator, which is described later, and each fraction treated according to its nature.

The next step depends on the amount and general appearance of the material made available by these preliminary operations.

In many cases, especially with non-asphaltic oils of low specific gravity, the sal ammoniac solution may appear only slightly opalescent or milky in appearance. Experience will dictate whether it is better to concentrate the suspended matter on a micro-filter, or to precipitate it directly on to a microscope slide by means of the centrifugal apparatus to be described later.

In the former case, the material on the micro-filter is transferred to the slide by back-washing and pressure in the manner to be described, and a temporary amount prepared for the microscopical search.

Usually sufficient quantity of organized material is collected to allow of several "spreads" for the search, and the complete examination of

these, together with the appplication and removal of reagents, the use of various methods of illumination and the logging of all significant objects discovered, constitutes the most tedious and time-consuming part of the process.

In the case of core samples, the sample is first disintegrated by soaking in water, and gently broken up with the finger, according to the ordinary procedure for collecting foraminifera.

In fact, the examination of the material for the smaller micro-fauna and flora is simply an extension of the latter process, in that it applies to the milky liquid which passes through the finest-meshed sieve of the foraminiferist, and is usually discarded.

The milky liquid is allowed to stand in a tall cylindrical vessel until the mineral matter has settled out, the supernatant liquid carefully decanted and micro-filtered by the same method as that used for oil.

With some clay-like core material which tends to give a persistent suspension, it may be necessary to add a flocculating reagent, due attention being directed to the effect of this on the density of the liquid and its possible chemical action on the micro-bodies likely to be present.

There is, however, a tendency for the flocculated mineral matter to carry down and retain some of the organized micro-bodies. This may sometimes be overcome by gentle stirring, or by reducing the air pressure on the liquid, when organized particles may rise with the expanding air-bubbles.

Oil sands present little difficulty as a rule: the sample is washed on a suction filter with suitable solvents to remove oil and bitumen, then with a little alcohol, and while still moist with the latter, washed with a 5 per cent. solution of sodium metasilicate.

The whole mass is then gently stirred into distilled water in a tall cylindrical vessel, the sand allowed to settle out and the liquid decanted. The density of the liquid may be adjusted if necessary by the addition of more metasilicate, in order to assist in the flotation or suspension of the organized material, which is collected on a micro-filter, as in the case of the organisms separated from crude oil.

## V. Apparatus and Manipulation.

### (a) *General Observations.*

In the general outline given in the previous section, it has been explained that the preliminary operations which lead to the final presentation of the micro-objects in a form suitable for examination and identification, comprise the following steps:—

(1) Dilution and straining of the oil to remove water, adventitious matter and coarse particles.

(2) Filtration of the diluted, strained oil through a water-soluble filter mass, which retains all the suspended micro-objects.

(3) Removal of oil, wax or bituminous matter from the water-soluble filter by means of appropriate solvents.

(4) Solution of the filter mass in distilled water, so as to release the micro-objects.

(5) Concentration of the micro-objects, combined with, when possible, their separation into groups of varying density.

(6) Transference of each concentrate, or group, to a microscope slide for examination.

*Step* 1.

With reference to the first step, sufficient detail has been given in the previous section to indicate the method of working and apparatus required, and it is only necessary to refer here to the possible presence of a certain amount of iron or steel particles, or of fragments of magnetic minerals from the formation, small enough in size to pass through the sieve.

Before passing to the next step, it is desirable and convenient to remove these from the diluted oil, and this can be done by stirring the latter slowly with a clean bar magnet, or more rapidly by pouring the oil through the space between the nearly touching flat extension poles of an electro-magnet.

In either case the magnet poles should be washed down with fine jets of solvent, delivered with some pressure from a pipette, in order to detach any non-magnetic particles which may have been trapped in the operation. The solvent chosen should first remove oily matter, and be followed by others which are found by experiment to fulfil the desired object, as observed by careful scrutiny with a lens. Chloroform followed by alcohol and then by a 10 per cent. solution of sodium metasilicate has been found effective by the author. The washings, or whichever of them are known to contain objects of possible interest, may then be passed to one of the micro-filters described in connection with step 5.

The material retained on the sieve in step 1 must not be overlooked. If it appears to contain objects which are not definitely recent or adventitious, it should be subjected to separate examination microscopically.

It is frequently possible to segregate the unimportant material by magnetic means, hand-picking with forceps or needles, or by gravity separation, as described below.

Before proceeding to describe in detail the special technique and apparatus for applying it in the second and succeeding steps of the method, it may be mentioned that the author has not been unaware of the very many and useful alternative methods which have supplied the rich literature relating to chemical microscopy.

Many of these have been tried, and while they have not proved so suitable for crude petroleum examinations as those developed by the author, it does not follow necessarily that they would be unsatisfactory in the hands of operators more accustomed to their use.

It is not suggested, therefore, that the methods and appliances about to be described represent the only ones available; but, in the opinion of the author, they do possess the merit of comparative simplicity, coupled with the fact that all the special appliances used can be made in the laboratory from relatively cheap material, and without any unusual degree of manipulative skill.

Throughout all the operations, it cannot be too strongly insisted upon that there is an omnipresent enemy in the shape of adventitious dust, and extraordinary measures are necessary to exclude its insidious entry into the microscopic evidence.

This is the more necessary because many of the ancient forms of microscopic life do not differ greatly in outward appearance from those of more recent existence.

Apart from the special pieces of apparatus described later, the ordinary equipment of a well-found chemical laboratory is suitable.

For the working bench a good light is essential, and it is desirable to have the table-top of glass or similar smooth-surfaced material which can be readily kept free from dust. In the author's laboratory the whole bench is fitted with a roll-top, which can be used entirely to cover it and any apparatus it supports during the times that it is not in use.

Small glass bell-jars are used to cover minor pieces of apparatus, and glass caps to place over the open orifices of any appliance while in use.

All solvents and reagents are kept in glass-capped vessels, with either glass or rubber stoppers; the use of corks is to be avoided. The working bench should be provided with connections to gas, water, electric current and vacuum supply systems. The vacuum required for the filtration operations need not be higher than 10 mm. of mercury; a vacuum gauge should be installed, and it is also convenient to insert a three-way tap into the vacuum system so that air may be admitted when necessary without disconnecting the apparatus.

For the transference of particles as described under step 6, a supply of compressed air, in small amounts but under controlled conditions, is required.

This can be provided conveniently by a small hand condensing syringe, with a non-return valve, clamped to the bench in a convenient position for the operator's left hand.

Minor appliances of general utility include a supply of small glass pipettes with jets of varying degrees of fineness, and fitted with rubber teats; they may vary in capacity from 1 to 5 ml.

There will also be required a supply of finely pointed sable-hair pencils. These should be of the highest possible quality, free from loose or broken hairs, and the greatest care should be taken to ensure their freedom from foreign matter. Before using them in the operations described under step 6, they must be scrutinized under a low power of the microscope while their hairs are spread by pressure on a glass slide.

They are best cleaned by twirling in alcohol in a porcelain dish, using one pencil to brush another. When perfectly clean they may be stored, while still moist, in glass tubes.

All glass apparatus should be freed from organic matter by the use of chromic acid mixture followed by washing with distilled water. This is specially necessary in the case of the micro-filters and separators described under step 5, in which a chemically clean interior wall surface is desirable.

For the smaller basins, dishes or capsules, it is convenient to use vitreosil or transparent silica, since they can be quickly freed from organic matter by ignition.

### (b) *Special Apparatus and its Use.*

*Steps* 2 *and* 3. *The Soluble Filter and its treatment.*

This is prepared from sublimed ammonium chloride of so-called C.P. quality. As commonly supplied in small fibrous lumps, it can be used if

known to be free from cork dust, cellulose fibre from paper wrappings or other extraneous matter. A blank test will determine this, and it may be necessary to re-sublime it.

The lumps should not be crushed or pulverized, but scraped with a narrow-bladed steel scraper in the direction of the fibre. The light feathery scrapings are packed into a small (10-ml.) transparent silica Gooch crucible, in small portions at a time, each addition being tamped down with a flat-ended glass rod until a filter bed about 4 or 5 mm. in thickness has been built up. The correct thickness and degree of compaction are a matter of experience, but the filter can be tested by very finely pulverizing some of the salt, suspending it in kerosine and passing the latter through the filter with the highest suction pressure available. The filtrate should be quite bright and free from suspended matter.

During the filtration of the diluted crude oil, the crucible should never be completely filled, about 2 or 3 ml. of liquid spare capacity being left for possible contingencies. The latter may comprise: (1) clogging of the filter mass by precipitation of asphaltic matter. This can usually be remedied by introducing about 1 ml. of carbon bisulphide by means of a pipette directly on the filter surface. (2) If the crude oil also contains wax, the evaporation of the $CS_2$ at the bottom of the crucible will sometimes cool it sufficiently to precipitate the wax, which will again stop filtration. The remedy in this case is to warm the crucible, and for this purpose the author uses a minute tubular electric immersion heater, 9 mm. in diameter, which is supplied with current from a low-voltage transformer.

A small 6-volt electric bulb on a special glass holder can serve the purpose equally well, and is easily washed down with solvent from a pipette.

Sometimes wax alone may separate from some crudes, in which case time may be saved by warming the whole bulk of oil previously.

After filtering the oil, its container is washed with repeated jets of kerosine from a pressure pipette, the washings being received in the filter crucible. No trace of sediment should be left.

The filter mass itself is then washed with kerosine until the filtrate is colourless. This may not remove all bituminous matter, however, and if by examination with a lens this appears to be present, the crucible should be half-filled with carbon disulphide, and left to stand without suction for a short time. The colour of the filtrate when suction is re-applied will indicate whether bitumen is being removed, and to prevent excessive cooling and deposition of moisture, the remaining half of the crucible should be filled with warm kerosine, and the two liquids sucked through the filter. This operation may be repeated if necessary and the filter then washed two or three times with petroleum spirit to remove the kerosine. Finally the last traces of petroleum spirit are removed by drawing a current of warm dry air through. This can be conveniently effected by suspending the little electric heater inside the crucible and continuing the action of the vacuum pump.

It will be noted that the solvents used have been petroleum products and carbon bisulphide only. If the latter had been omitted, the micro-objects on the filter would not have been in contact with solvents differing essentially from those in the original crude. If at this stage other solvents

are applied, it may be possible to extract from some of them resinous materials or colouring matters which might provide preliminary information as to their nature.

This can sometimes be made use of for correlation purposes. For instance, if an oil from a known source is found to contain the remains of coniferous wood and a resin which is identifiable, the filter mass from a second oil could be treated with a solvent for that resin, which, if found and shown to be identical with the resin of the first oil, would indicate a possible common source for the two oils. This correlation would be further strengthened if microscopical examination of the second oil showed the presence of similar coniferous wood remains.

The difficulty in applying this principle arises from the extremely minute quantities of material extracted. Nevertheless, sufficient may sometimes be obtained to give a distinctive odour after evaporating off the solvent, and even to give a colour reaction.

*Step* 4. *Solution of the Filter-Mass.*

The crucible with its oil and solvent-free filter-mass is placed in a small beaker, and jets of warm distilled water are applied to the filter-mass by means of a pipette.

The water is allowed to percolate through the mass, the crucible being lifted with forceps to allow the liquid to drain through. Successive quantities of water are applied until all the sal-ammoniac dissolves, and the particles originally held by the crude oil are washed through the perforations of the crucible bottom into the beaker.

Moving the crucible up and down with the forceps assists the process. Sometimes a slight scum will tend to creep up the sides of the crucible; this must be washed down with a fine stream of alcohol from a capillary pipette, using the minimum quantity necessary.

If the scum is dark coloured, and tends to float on the liquid, it is probably lignite, coal or carbonized plant material.

Occasionally particles may be observed which will not pass through the perforations. These may be extraneous material which has escaped the preliminary straining; cotton-waste fibres often appear at this point. The particles should be carefully examined with a hand lens, and if obviously not of recent origin, may be washed out of the reversed crucible. In case of doubt it is preferable to wash them into another vessel for concentration separately on a micro-filter and subsequent microscopical examination.

The appearance of the final solution of sal-ammoniac, when cooled to room temperature, may vary greatly with different crudes. If it shows only a faint opalescence or turbidity and little or no indication of heavy particles settling out at the bottom, it may be better to concentrate all the particles on micro-slides by the centrifugal method.

More frequently, however, there is seen to be considerable difference between the densities of the particles, and the use of one of the micro-separators and filters is indicated.

It occasionally happens that all the particles settle rapidly to the bottom of the vessel with apparently no material left in suspension. In this case the supernatant liquid may be carefully decanted off and passed through a micro-filter. The sediment is then washed thoroughly by decantation,

first with water, then with alcohol, and finally dried in a gentle current of warm air.

The dried sediment may then be transferred to an organic solvent in one of the separators. By the use of mixtures of carbon tetrachloride and chloroform it is possible to separate the organic from the mineral or fossilized material with fair success.

*Step* 5. *Concentration and Separation of Particles.*

The methods available for this step may be considered under two headings:

(1) Separation by gravity, and micro-filtration.
(2) Centrifugal concentration, which combines steps 5 and 6.

(1) *Separation by Gravity.* Under the first heading the construction and use of micro-separators and filters merit special description, since they are not procurable from supply houses, and must be made by the operator.

The appliances are of varying forms and dimensions, each suited to the particular conditions which may arise when examining crude oils of differing character.

Some useful forms are shown in Figs. 1 to 6, and the special application of each will be described later.

The special feature in all of them is the use of a disc of porous porcelain as the filtering medium. This material can be permanently sealed into soft soda glass as ordinarily used in the laboratory, but not into pyrex, monax or similar types of hard glass.

It is sufficiently close in texture to hold back the finest particles, and is very easily worked into shape by grinding on a carborundum wheel. Its advantage over sintered glass lies in its cheapness, and the fact that after use a clean, fresh filter surface can be provided by scraping or grinding off the old one. This can be done many times before the disc becomes too thin to resist the filtration pressure.

The discs may vary in diameter from 4 to 15 mm. and in thickness from 1 to 4 mm., according to the size of filter. The ordinary white "biscuit" porous porcelain tile as used in the laboratory for draining crystals serves as raw material for making them. Chips or flakes are used for the smaller sizes, while rough blanks, cut by grinding with a notched steel tube and carborundum powder, serve for the larger ones.

Each disc is ground to circular form by holding against the revolving carborundum wheel, and then reduced to uniform thickness in the same manner. The edges are ground to an angle which conforms approximately to the shape of the glass tube for which it is destined, and to aid in the sealing operation a shallow groove is made on the periphery with a carborundum file which also serves to shape the disc to a close fit in the tube.

The sealing operation is performed with a narrow horizontal blowpipe flame, the glass tube being held vertically, and slowly revolved in the flame, the porcelain disc being supported by a carbon pencil passing upwards inside the tube.

As soon as the glass softens it is gently dabbed with a pointed carbon pencil at one or two places, so as to indent the glass and drive it into the

groove on the edge of the disc. This holds it in place, and the supporting pencil is withdrawn.

Heating is then continued with continual rotation of the glass, until the latter forms a close seal with the edges of the disc. Very slow cooling completes the operation.

For grinding away a used surface a small flat-edged carborundum pencil can be used, or a narrow chisel-ended scraper of steel, the powder and scrapings being removed by a small bristle brush and by a blast of air.

FIG. 1.

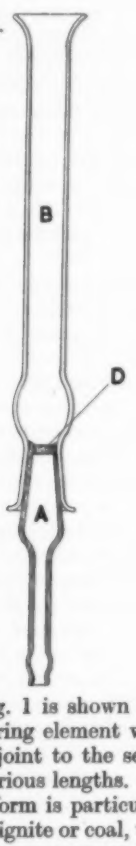



FIG. 2.

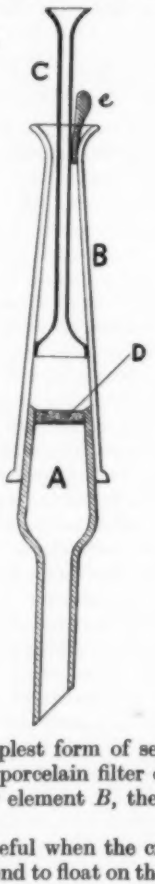



FIG. 3.

In Fig. 1 is shown the simplest form of separator-filter, in which *A* is the filtering element with its porcelain filter disc *D* fitting by means of a ground joint to the separator element *B*, the tubular part of which may be of various lengths.

This form is particularly useful when the crude oil contains substances, such as lignite or coal, which tend to float on the surface of the sal-ammoniac solution as a scum or film.

Such substances are liable to hold traces of oil or wax rather persistently, and this may be taken advantage of in effecting their separation from other micro-bodies, since not only do they float, but during the descent of the column of liquid in the tube *B* they adhere to its walls, and remain there while the remaining particles are collected on the filter disc *D*.

After the filtration, the two parts of the apparatus are separated, the particles on *D* washed with distilled water and removed by the method to be described later. The two elements are then reunited and the particles adhering to the walls of *B* washed down with jets of alcohol applied by a fine-pointed pressure pipette.

If desired, these particles may be separated by gravity into heavy and light fractions, by adjusting the density of the liquid in *B*, or they may all be collected on the filter-disc by suction, and removed from it for microscopical examination.

Fig. 2 shows a more elaborate form of separator, in which provision is made to avoid settlement of particles on the walls of the tube and to separate heavy from light particles in a systematic manner. It is of general utility when the amount of suspended matter is large, and there are obvious differences in the density of the particles.

As will be seen from the figure, the hollow plunger *C* with its lower conical expansion can be drawn upwards and wedged by the little rubber wedge *E*. This cuts off the lower zone of settling particles and allows them to be collected on the filter disc *D* by suction, air entering through the tubular stem of *C* to take the place of the liquid withdrawn by filtration.

Water for washing these particles can also be applied through *C* without disturbing the density of the liquid in the upper zone.

After separating the two parts of the apparatus and removing the particles on the filter disc, the apparatus is reassembled and the plunger *C* released. The density of the liquid may then be readjusted by suitable additions of alcohol or water to complete its original volume, and the plunger drawn up again and wedged as before, the new crop of particles being collected on the filter disc. This operation may be repeated as often as may be necessary to divide the material into crops of differing density.

The enlarged end of the plunger *C* must be carefully ground to make a tight joint with the walls of the tube, but grease must not be used to assist this. Care should be taken to avoid trapping suspended particles in the joint, this being usually effected by twirling the stem rapidly with the fingers just before contact is made. When adjusting the density of the liquid, the plunger in its lowered position can be used as a stirrer.

In Fig. 3 is shown a modification of Fig. 2; it is used in the same way, and is useful when particles are present which tend to adhere to the tube walls under the conditions mentioned in connection with Fig. 1. It may be mentioned that in this form, but provided with a fine-meshed sieve instead of the porcelain disc, the separator can be used for separating light and heavy mineral particles from core samples.

In cases where the particles from the primary soluble filter show little tendency to settle out, it may be preferable to collect them by upward filtration using the form of filter shown in Fig. 4. The short projecting branch *A* is fitted with a rubber stopper, and before removing the particles from the filter surface *D* by air pressure applied to the long arm *B*, this branch serves to empty the apparatus, introduce another liquid above the filter, and by means of the rubber stopper release the pressure at will.

The very small micro-filter shown in Fig. 6 is of different construction;

the filter tube *A* and liquid container *B* are ground at the ends so as to form even contact at their abutting surfaces, a short rubber sleeve serves to connect them.

FIG. 4.

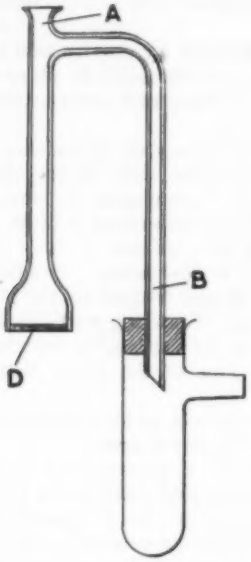
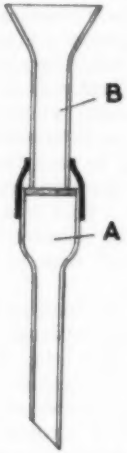



FIG. 5.




With this form, the particles in a temporary mount on a micro-slide can be collected, treated with a chemical reagent or selective stain, or washed free from the mounting medium and returned to the slide again.

FIG. 6.

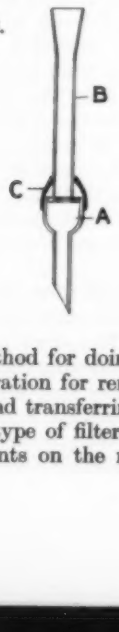
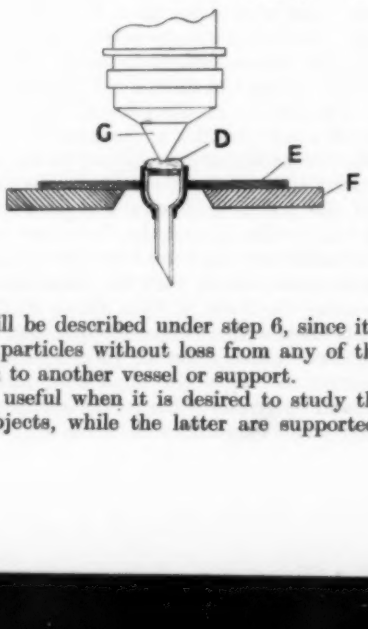



FIG. 7.




The method for doing so will be described under step 6, since it includes the operation for removing particles without loss from any of the micro-filters and transferring them to another vessel or support.

This type of filter is also useful when it is desired to study the action of reagents on the micro-objects, while the latter are supported on the

white background of the filter disc, and the " dipping cones " of the Ultropak objectives are employed.

For this purpose the rubber sleeve *C* (Fig. 6) is slipped down outside the filter-tube after the particles have been collected on the disc and the tube *B* has been removed. The upper margin of the sleeve should project slightly above the level of the disc so as to form a shallow receptacle for the reagent.

To support the arrangement a $3'' \times 1''$ strip of ebonite *E* (Fig. 7) rests on the microscope stage *F*, being held in the grip of the mechanical stage.

A hole in the ebonite strip is of sufficient size to accommodate the filter-tube, with its rubber sleeve, the latter passing through the hole with slight friction, thus allowing the tube to be tilted slightly in any direction for levelling purposes. As shown in Fig. 7, the cone of the objective dips into the drop of reagent *D*, while the filter disc can be moved bodily, with its support by the mechanical movement of the stage.

It is not always necessary to remove particles from a slide for chemical

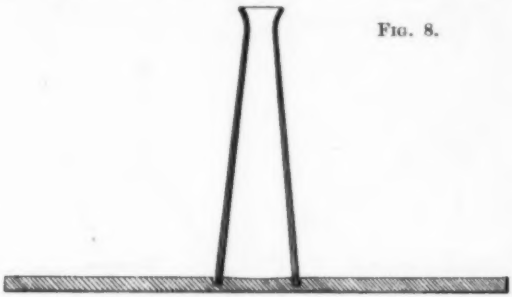


FIG. 8.

treatment or staining, since it is obviously possible to apply the reagent in the conventional manner to one edge of the cover-glass and draw the liquid away from the opposite edge by filter paper. Sometimes, however, the mountant is incompatible with the new reagent, and must be removed, even although this means that the particles will all be mixed up and must be found by a fresh search.

(2) *Centrifugal Concentration*. For this method specially constructed precipitating vessels adapted to the micro-slides must be made, and also a special form of centrifugal head and corrier to support them.

The slides are of the type used in biological work for hanging-drop cultures. They have a central, slightly concave disc, surrounded by a deep annular groove.

Short lengths of glass tubing slightly smaller in inside diameter than that of the central disc, and of a wall thickness to fit into the groove, are drawn out so as to form conical vessels, about 5 cm. in height. The wider ends are ground flat, and square with the axis of the tube, and then, by careful grinding with fine carborundum powder, they are made to fit over the outer edge of the central slide disc and at the same time fit snugly into the annular groove. Fig. 8 shows a sectional view of the assembly, and Fig. 9 the centrifugal head and carriers for the completed

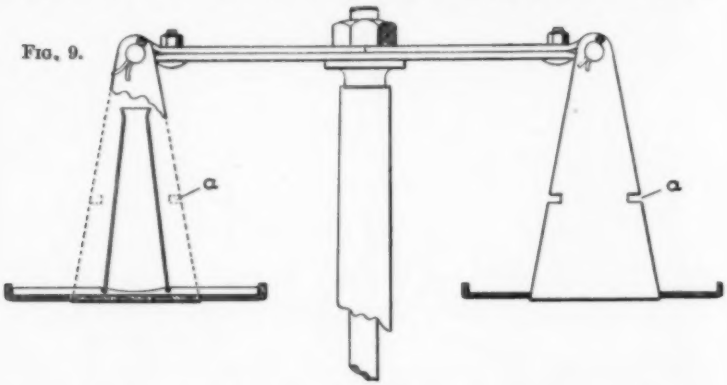
slides, which should be made in pairs of equal weight. The notches *aa* shown on the carriers are for rubber bands which support the tubes when starting and stopping the machine.

The centrifugal head is made of sheet aluminium, the flat pieces which are riveted to the swinging stirrups have turned up ends so as to accommodate exactly the slides and permit the latter to lie perfectly flat on their surfaces.

In using this apparatus, the central disc of each slide is very lightly coated with a slightly sticky medium such as gold-size. The lower rims of the tubes are also given a coating with the same medium, and the tubes pressed into place so as to make water-tight joints with the central discs.

The liquid with its suspended particles is divided into two parts of equal volume which are poured into the tubes. After placing in the carrier and centrifuging for several minutes, all the particles are driven on to the discs to which they adhere. After stopping the machine, the

FIG. 9.




perfectly clear liquid is removed from the tubes with a pipette. By warming the slides slightly, the tubes are then detached and the slides are ready for microscopical examination. Owing to the concave form of the disc surfaces, there is a tendency for the particles to concentrate in the centre, but care should be taken not to overlook in the examination any that may have been trapped at the edge.

*Step* 6. *Transference of Micro-Objects to Slides.*

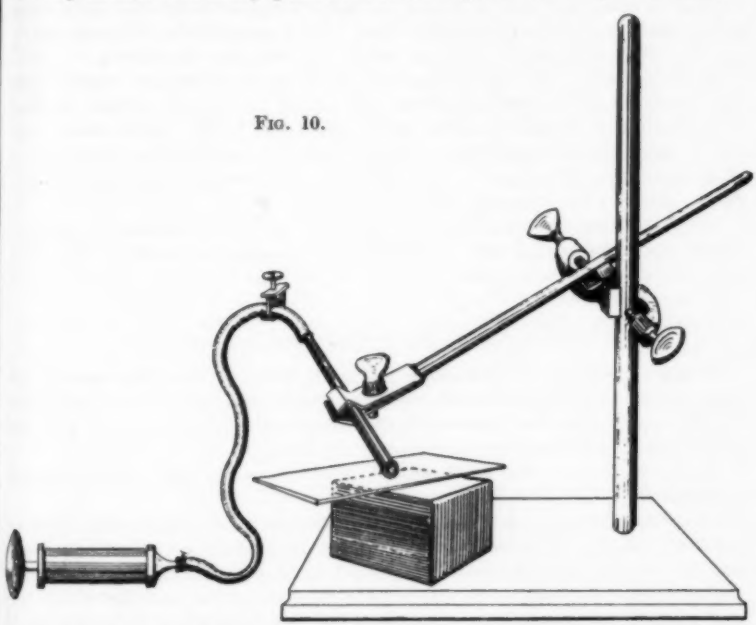
This is a very delicate operation, and should be performed in a good light, and with the aid of a good hand magnifier.

The filter tube with the particles retained on its disc is removed from the rubber stopper of the filtration flask and supported by a small clamp and retort stand, so that the filter disc is downwards and the tube inclined at an angle of 45°. The microscopic slide is supported on a wooden block so that its centre is just beneath the lower rim of the filter disc, but not touching it. By means of a pipette a few drops of liquid (water, alcohol, or dilute glycerol) are introduced into the filter tube so as to form a short column above the porcelain disc.

The tubular end of the filter is then connected to the condensing syringe, referred to in paragraph (*a*), by medium-walled indiarubber tubing, about 8 inches long. The connections to tube and syringe are firmly bound with wire or waxed thread, and a small screw clamp is placed on the rubber tube close to its junction with the filter tube. Fig. 10 shows the complete assembly.

With the clamp tightly closed, air pressure is built up inside the rubber tubing by one or two strokes of the syringe, and the surface of the filter-disc is observed with a lens while the clamp is slightly opened. As soon as the first signs of moisture appear on the disc, the clamp is closed again, and by means of a finely pointed sable-hair pencil the tiny filter cake of

FIG. 10.



particles is gently detached from the disc and guided to its place on the slide. Sometimes the particles do not come away in a single mass, but tend to break up, in which case, by manipulating the clamp and pencil, it is possible to obtain a single drop of liquid, thickly charged with particles, which is guided on to the slide as before.

It may be necessary in this case to transfer several drops on successive slides before the filter-disc is entirely free from particles.

In using the pencil, only the extreme point is used, and every endeavour is made to avoid charging it unduly with particles; at the conclusion of the operation it may be washed with a fine jet of alcohol into a small dish, the alcohol evaporated at a low temperature in a gentle current of air, and the dry particles swept on to the slide.

Dilute glycerol is a useful temporary mountant for the particles, and if

$\frac{3}{4}$ inch square cover-glasses are used, the " spread " may be kept in position by a narrow streak of thick celluloid varnish on the two edges parallel to the sides of the slide, the other two edges being left open for the application or withdrawal of reagents, stains, etc.

It may be mentioned that the colour of the deposit on the filter disc is often characteristic of a particular crude, and is worth recording, grey, black, brown, reddish-brown, yellow and brick red being the usual shades, but grass-green and bluish-green are sometimes observed.

As mentioned above in connection with the small micro-filter shown in Fig. 5, it is possible to remove the particles from a slide and, after treatment by solvents, reagents or stains, transfer them back to the slide.

This is done by first separating the cover-glass from the slide, and gently washing the particles from them into a small dish with a capillary pipette and fine jets of a solvent which does not attack rubber.

From the dish, first the solvent and then the particles are washed into the funnel tube *B* of the micro-filter, and during continually applied suction to *A* gradually washed down on to the filter disc. The rubber sleeve and funnel are removed and given a further precautionary wash down into a dish, any particles found being guided on to the filter disc with single drops of liquid from the pipette.

After treating the particles on the disc with the required reagents, applied in single drops from a pipette, the transference back to the slide may be effected in the manner already described.

## VI. Microscopic Equipment and Accessories.

Owing to the very large number and variety of objects which have to be scrutinized, and if possible identified by mere inspection, it is important for the microscopist to have available for instant employment all possible means which are likely to assist him in his work.

Consideration of this kind should determine the type of microscope most suitable for the work.

Thus the illumination of the object by transmitted ordinary light either axial or oblique, by polarized light under orthoscopic or conoscopic conditions, and by reflected light giving axial, inclined or annular illumination, should ideally be capable of application at any instant, without the delay and change of adjustment occasioned by the necessity of fitting some accessory into the substage or body-tube of the instrument.

Additionally to the above, it may be necessary to examine an object by ultra-violet light, by conditions of dark-ground illumination, by transmitted or reflected light of different colours, and occasionally when maintained in an electric or magnetic field.

The so-called " Universal " type of microscope does not meet the case entirely, since the change from a biological to a petrographical assembly is effected only by the removal of one body from the stand and substituting another, a distracting and time-consuming device, although undoubtedly the arrangement provides for each assembly the conditions of maximum efficiency.

The author has met the difficulty by the use of two microscopes, one, on which the greater part of the search is performed, being a fully equipped

biological instrument, but with the graduated, centring rotatory stage, and tube analyser of a petrographical microscope. The polarizing prism is a special feature. It is an Ahrens prism of very wide aperture (25 mm.), which is placed just below the secondary iris of the aplanatic substage condenser on a swinging mount. Thus the full aperture of the condenser can be utilized with polarized light, and the change from ordinary to polarized light is made instantly by a touch of the finger.

With this instrument, illumination by reflected light is provided by a small spot-light on an adjustable stand, placed at the side of the stage. Convenient to the hand of the operator are two switches which turn on transmitted or reflected light at will. The spot-light mounting is provided with slots for the insertion of coloured screens, which can also be inserted in the substage.

The second microscope is of the metallurgical type fitted with the Leitz Ultropak illuminator, which needs no description. Unlike the conventional type of metallurgical stand, this has been fitted with a substage condenser and illuminator for transmitted light as well. This avoids the necessity of transferring a preparation under examination with the Ultropak back to the other microscope, if a view by transmitted light is required.

This microscope is used for a general survey of a preparation, and is of special value also in examining deep-seated structures.

Both microscopes are fitted with graduated mechanical stages; an essential adjunct for logging objects discovered during the systematic search of each preparation.

The observation of fluorescence under ultra-violet irradiation can be provided for in a variety of ways, and has been the subject of considerable study. The indications are that it may furnish a means for differentiating between recent and ancient organized material, if combined with the application of suitable sensitizing agents or fluorochromes. The study has not advanced sufficiently to allow a description of the methods and results so far achieved to be included in the present paper, but it is hoped to make this the subject of a later communication.

It sometimes happens that dull black or grey and even sub-metallic particles are found in a preparation, and some doubt may arise as to whether they may not be mineral particles which have escaped the separating process. Even steel and iron fragments occasionally appear in the final preparation, having escaped the preliminary magnetic treatment. It is convenient, therefore, to have at hand a method for determining whether the particles are magnetic, or possess polarity.

A very small electro-magnet has been devised for this purpose, and is shown in Fig. 11. It is small enough to rest directly on a $3'' \times 1''$ slide, and its extended pole pieces place the objects under examination in a powerful magnetic field, while the magnet itself does not interfere with the focusing of an objective. A length of light flex connects the magnet to a battery, and a small through-way switch in the circuit permits the current to be turned on or off while the objects are under observation.

With reference to the method of observation, little can be said, since this depends on the individual experience of the operator. In general terms the procedure followed by the author consists first of a general survey of the preparation with the Ultropak, any objects of apparent interest being noted and logged.

The slide is then transferred to the other microscope, and by means of the mechanical stage systematically searched in horizontal strips. During the search the fine adjustment of the instrument is constantly in use, focusing each field as it appears, and also looking for objects in different planes of view. The proportion of unimportant matter is often very large, and it is easy to miss very transparent and colourless objects, such as the chitinous remains of insects or crustaceans, the bleached vestiges of cuticle, fronds of feathers, etc. From time to time polarized or reflected light is brought into play as required to assist in identification, and a note is made on the log when the application of a reagent for cellulose, lignin, suberized tissue, cutin or other material appears desirable.

The micrometer eyepiece is kept at hand in readiness to determine the principal dimensions of any object in which size and shape are important factors for identification purposes.

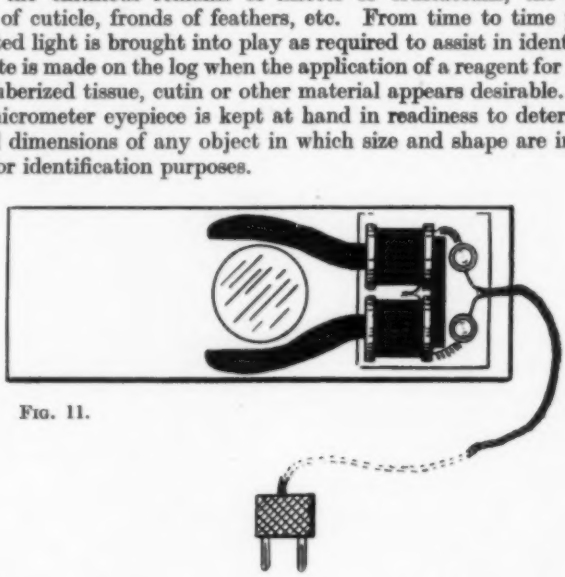


FIG. 11.

Occasionally, it may be necessary to transfer the slide to the other microscope for examination by the Ultropak illuminator or by ultra-violet light.

Although the method has not as yet been developed on a quantitative basis, it is desirable to record in the log some data relating to the frequency with which the same or similar objects occur. This is sometimes useful for correlation purposes. The characterization may be made on broad general lines, such as the relative occurrence of marine or terrestrial flora and fauna, or more specifically on the number of times some ubiquitous element from the animal or vegetable kingdoms appears in the preparation.

In the course of the examination, a large amount of mineral matter will be encountered, and this should not be disregarded entirely, although it is probable that the major portion will be easily recognizable as of no importance. On the other hand, it is worth noting and recording any mineral fragments which may have a possible relation with the source or reservoir formation of the oil, and also those which appear to be characteristic of certain types of oil. The tiny spherulitic particles of Pyrite seem always to accompany asphaltic oils of high sulphur content, often together with marcasite. The occasional presence of volcanic glass, or tufas, may

have a certain significance. Obviously there is likely to be present in the heavier fractions of the material recovered from the oil much material of interest to the sedimentary petrologist, but it would be outside the scope of this paper to deal with this aspect of the matter at issue.

It should be recognized, however, that not all the organized material present will be in a state of organic preservation; very frequently it may be completely or partly petrified, or yet again merely coated with mineral matter sufficiently to bring it into the heavier fractions of the separation process.

Moreover, certain elements of plant or animal structure may owe their decay-resistant character partly to the fact that they have acquired mineral additions during their life, and partly to their impregnation with petroleum after death. The author has found several examples of this duplex type of preservation. Sometimes also mineralization appears to take place in certain favoured localities of an organized structure, the surrounding tissues being preserved almost intact by the petroleum. If the mineralized portions become detached and isolated from the preserved organic portions, they may be difficult to recognize as parts of an originally organized structure, and this possibility should be kept in mind when surveying the mineral components of a preparation.

For recording purposes, and future reference, the conventional methods of photomicrography or camera-lucida drawings are available, and need no description. Both methods, however, are somewhat time-consuming. There are several excellent eye-piece cameras available which can be brought into action without greatly disturbing the adjustment of the microscope; but they require a series of distinct and separate operations on the part of the operator, who must clamp them in position, focus on a screen, or by means of a special device manipulate a dark slide, and after exposure remove them, before the business of searching a preparation can be proceeded with.

Moreover, there is a further consideration of special application to the microscopy of crude oils, in that the actual objects of interest are very small and usually few and far between. There may be as many as fifty or more which it is desirable to photograph in a single preparation, and very rarely will any number of them appear in the same field of view. This means in effect a large expenditure in plates, and the quite unnecessary inclusion of a great many unimportant objects in each picture.

To overcome this, the author has devised a special apparatus for selective photomicrography, which can be attached to the microscope, and does not interfere with the normal use of the instrument, whether inclined or upright. During the search of a preparation, any interesting object can be immediately photographed by itself, by merely turning a reflecting prism into a new position and manipulating a shutter.

The photograph is taken on 16-mm. film capable of recording thirty-six different objects, and a simple form of carrier has also been devised whereby four or six pictures can be taken on a single $2\frac{1}{2}'' \times 1\frac{5}{8}''$ plate.

A sectional view and description of the camera is shown in Fig. 12, and it may be mentioned that the photographic lens $P$ has a focal length so chosen, that, in combination with the sliding tube $T$ which carries the film holder, it acts as the lens of a camera focused for "infinity."

Thus, any object focused by the microscope for the eye of the observer will be in focus on the film when the prism *B* is turned into the position for making an exposure.

If, however, it is desired to increase the magnification by extending the tube *T*, this adjustment is disturbed, and it is necessary to focus the image. This can be done by a little magnifier and screen which is shown

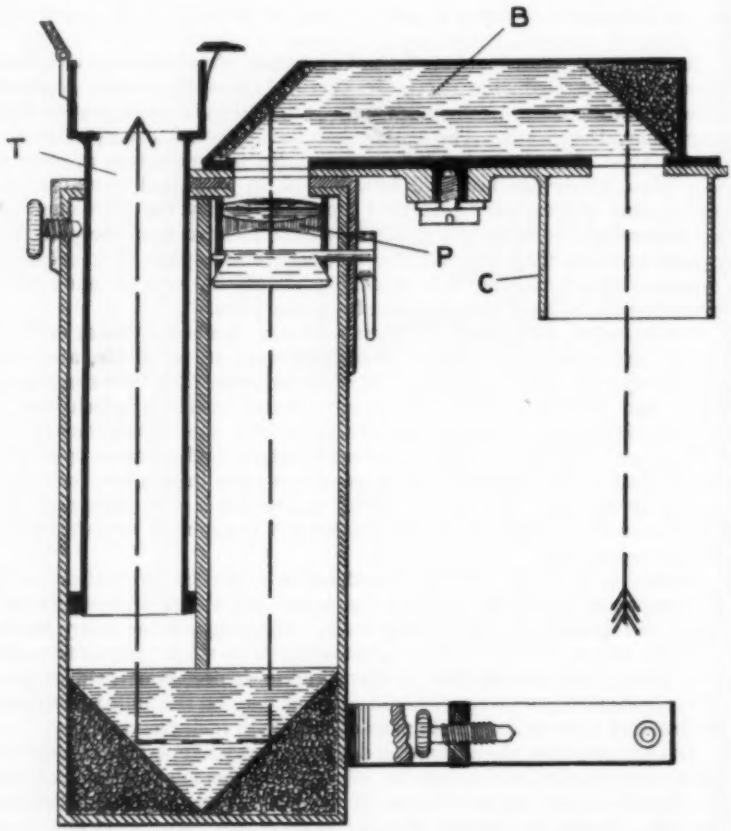



FIG. 12.

erected in Fig. 13 (prism *B* in " observing " position) and folded down out of the way of the film holder in Fig. 14 (prism *B* in " exposing " position). Usually the magnification is sufficiently secured by the former arrangement, and in any case is alterable by changes in the objective or ocular. The whole assembly weighs only 15 ounces, and since the cap *C* fits over any standard ocular, it does not interfere with any optical combination likely to be required.

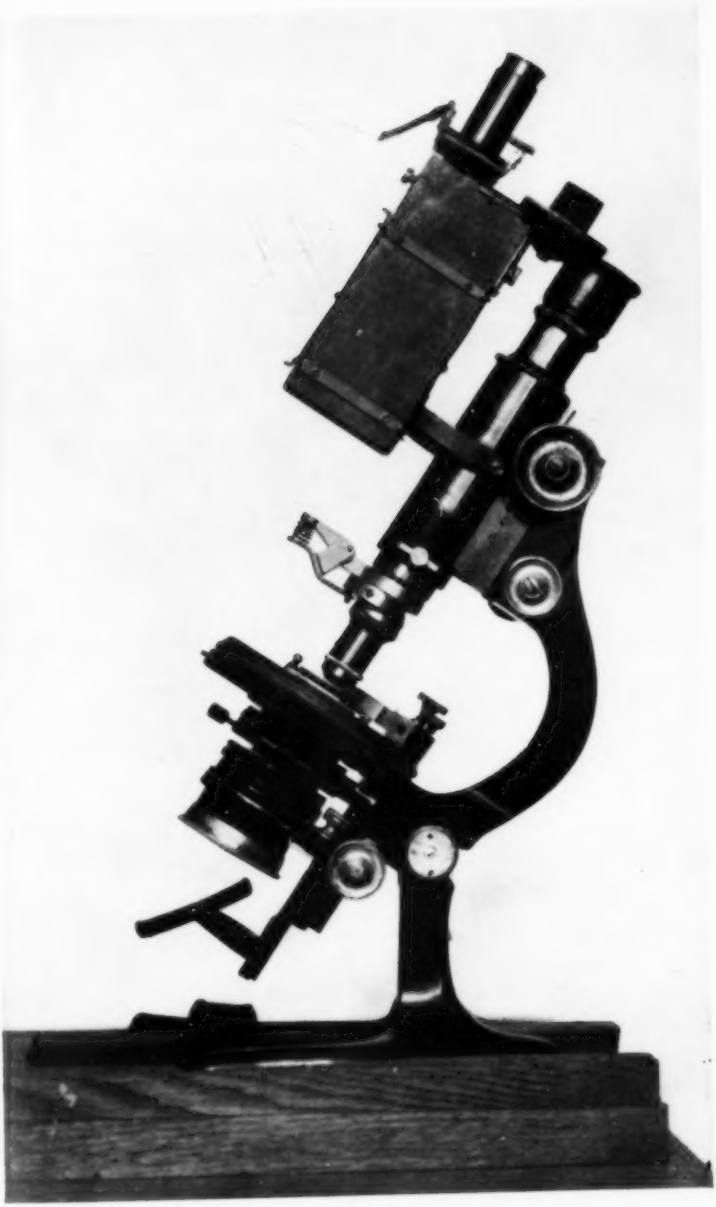


Fig. 13

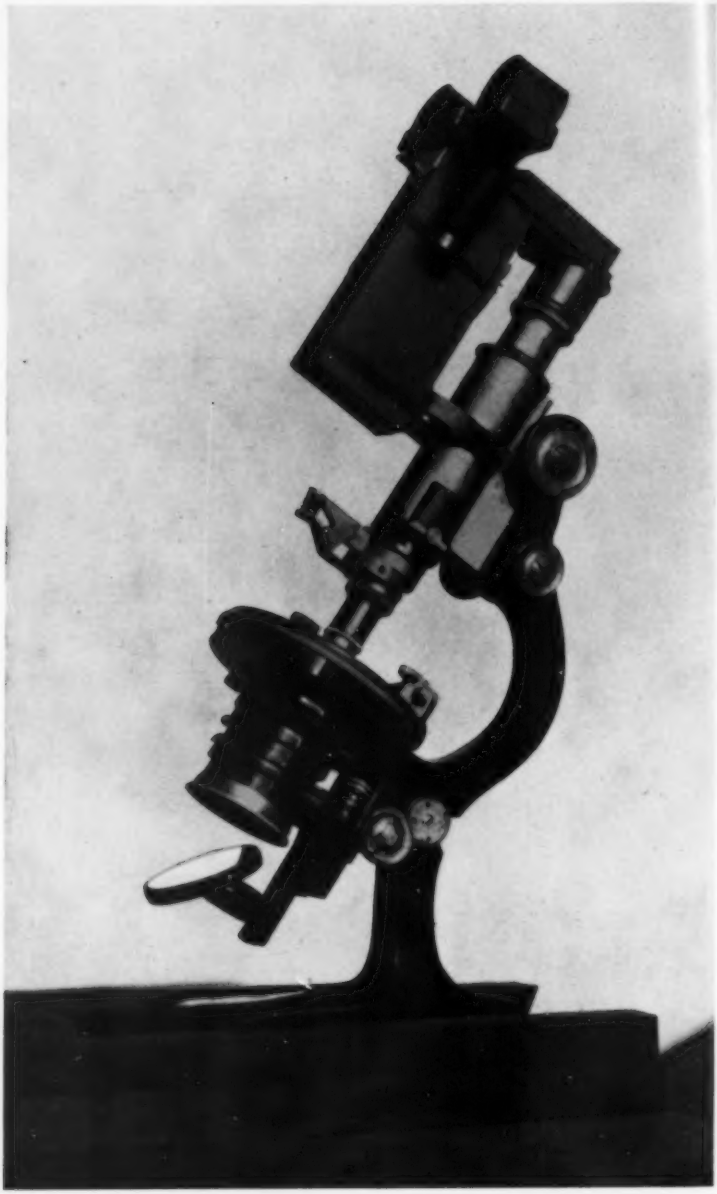


Fig. 14

# MICROSCOPICAL EXAMINATION OF CRUDE PETROLEUM

## PART II

## Practical Results and Observations

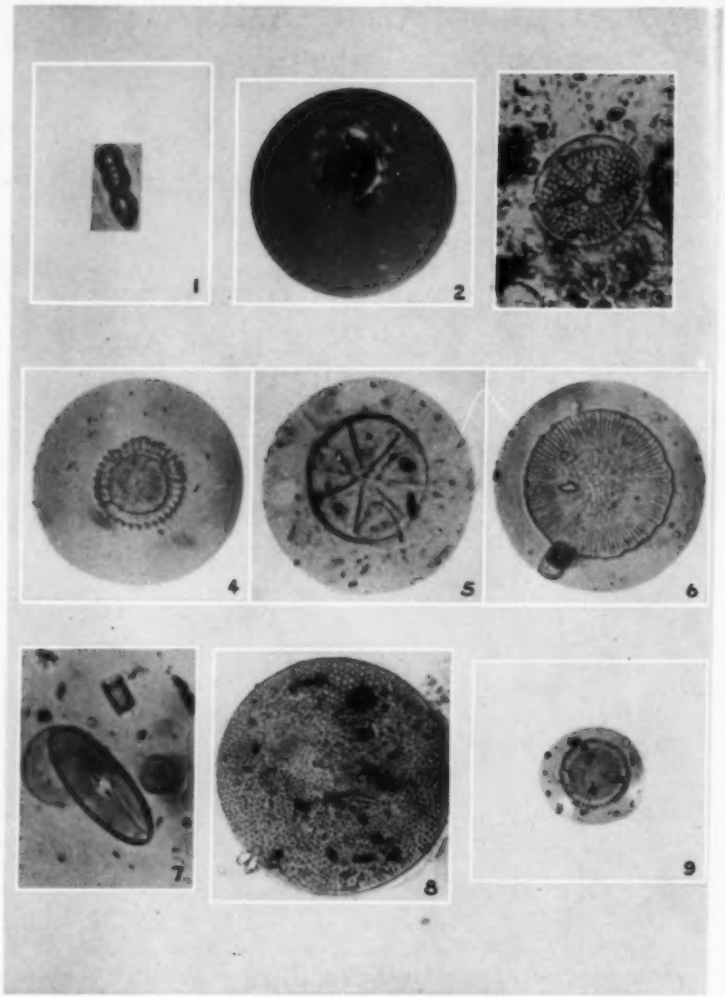
PLATES I–XVII

*NOTE*

The magnifications stated are those given in the original microphotographs of the Author.

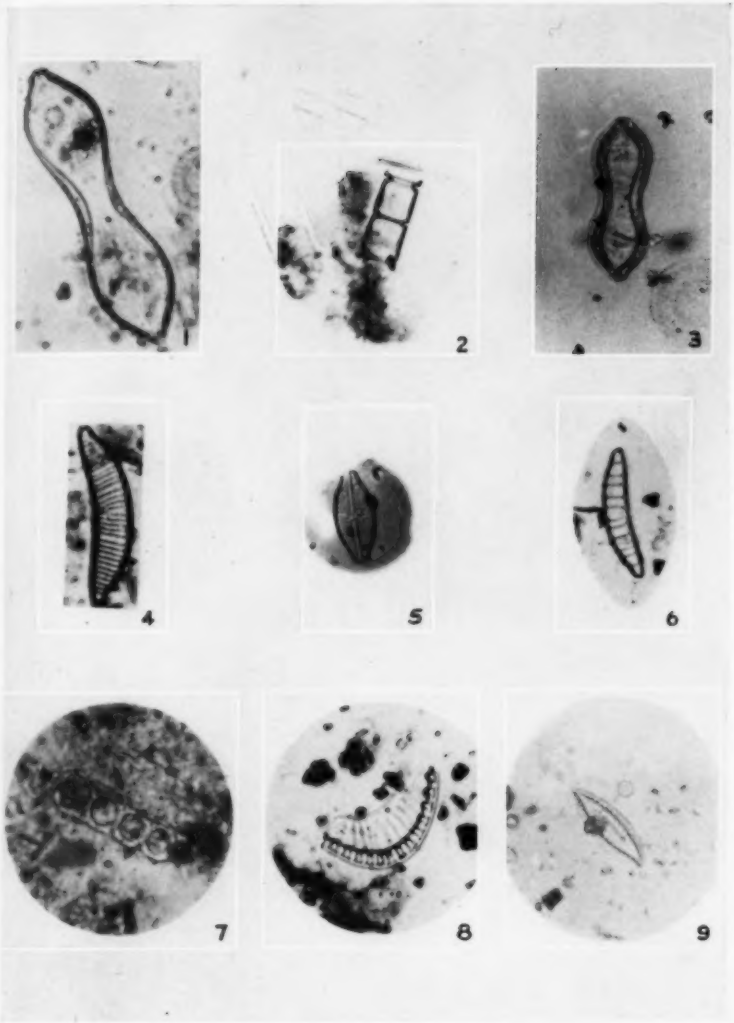
Plates I-XIII have been reduced to $\frac{1}{4}$ and Plates XIV-XVII to $\frac{1}{5}$ of their original size.

PLATE I.



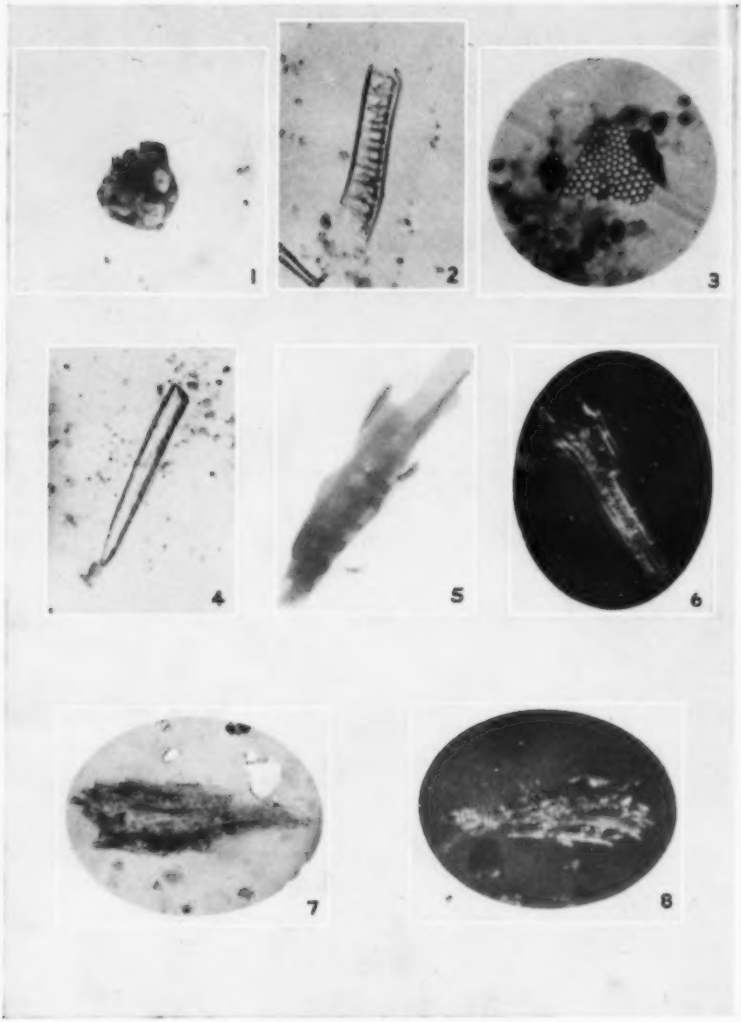

1. Foraminifera, Miocene oil-sand, Filisola, Mexico. (× 25.)
2. Pyrite globules embedded in partly mineralized cell from Miocene oil, Filisola, Mexico. (× 320.)
3. Diatom from Miocene oil, Tonala, Mexico. (× 640.)
4. ,, ,, Cretaceous oil, Huitzalté, Mexico. (× 560.)
5. ,, ,, Miocene oil, Tonala, Mexico. (× 640.)
6. ,, ,, Cretaceous oil, Huitzalté, Mexico. (× 560.)
7. ,, ,, Cretaceous oil, Furbero, Mexico. (× 640.)
8. ,, ,, Miocene oil, Tonala, Mexico. (× 376.)
9. ,, ,, Cretaceous oil, Huitzalté, Mexico. (× 560.)

PLATE II.



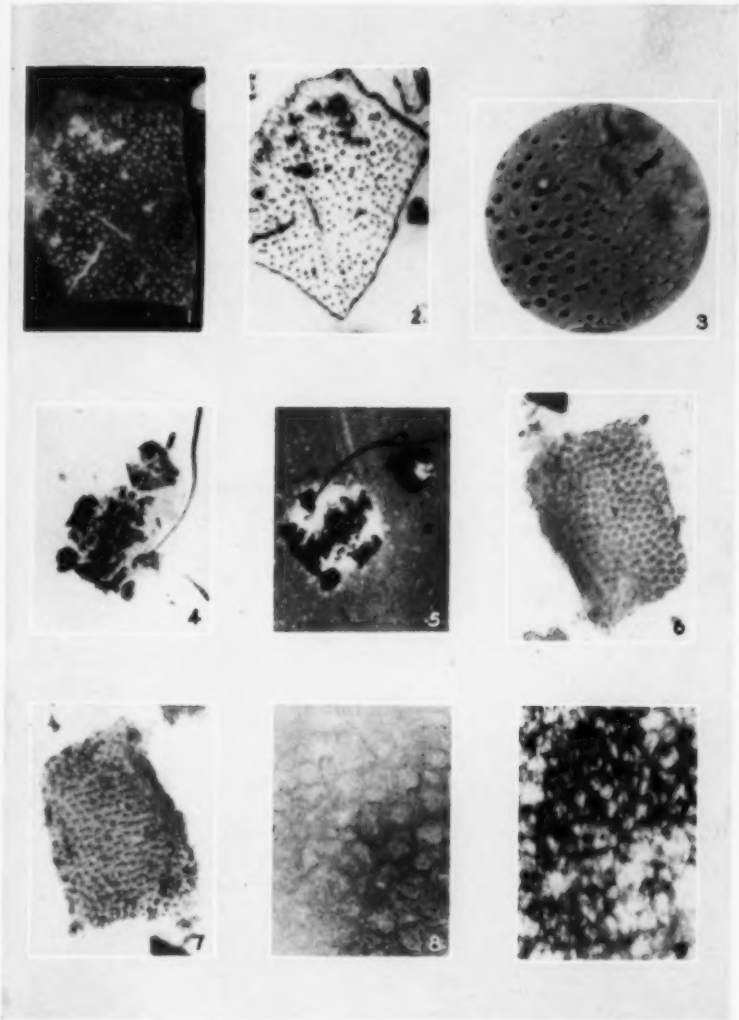

1. Diatom from Cretaceous oil, Huitzalté, Mexico. (× 560.)
2. „ „ Cretaceous oil, Huitzalté, Mexico. (× 560.)
3. „ „ Cretaceous oil, Furbero, Mexico. (× 376.)
4. „ „ Miocene oil, Belem, Mexico. (× 480.)
5. „ „ Cretaceous oil, Huitzalté, Mexico. (× 560.)
6. „ „ Cretaceous oil, Furbero, Mexico. (× 640.)
7. Radiolarian fragments, Eocene oil, Tlacalula, Mexico. (× 640.)
8. „ „ Eocene oil, Tlacalula, Mexico. (× 480.)
9. „ „ Cretaceous oil, Furbero, Mexico. (× 200.)

PLATE III.



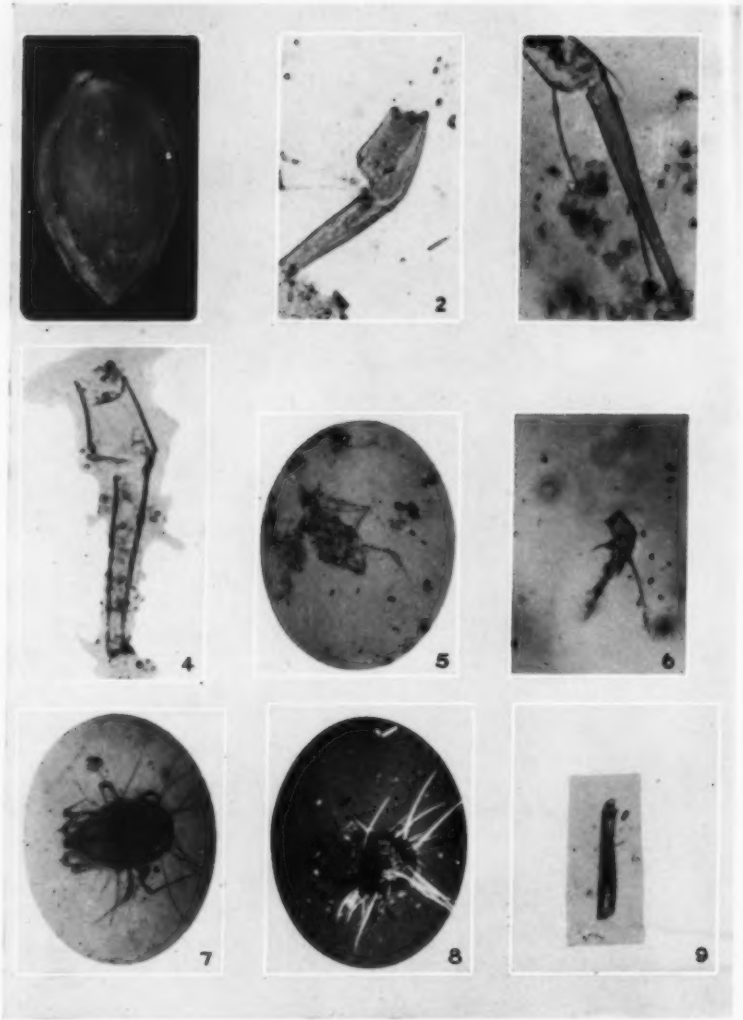

1. Radiolarian fragments, Eocene oil, Tlacalula, Mexico. (× 324.)
2. „ „ Cretaceous oil, Furbero, Mexico. (× 376.)
3. „ „ Cretaceous oil, Furbero, Mexico. (× 480.)
4. „ „ Miocene oil, Tonala, Mexico. (× 376.)
5. Petrified wood, Pliocene oil, Moreni, Roumania. (× 376.)
6. „ „ Eocene oil, Tamantao, Mexico. (× 120.)
7. „ „ Miocene oil, Assam. (× 128.)
8. As No. 7 by polarized light. (× 128.)

PLATE IV.



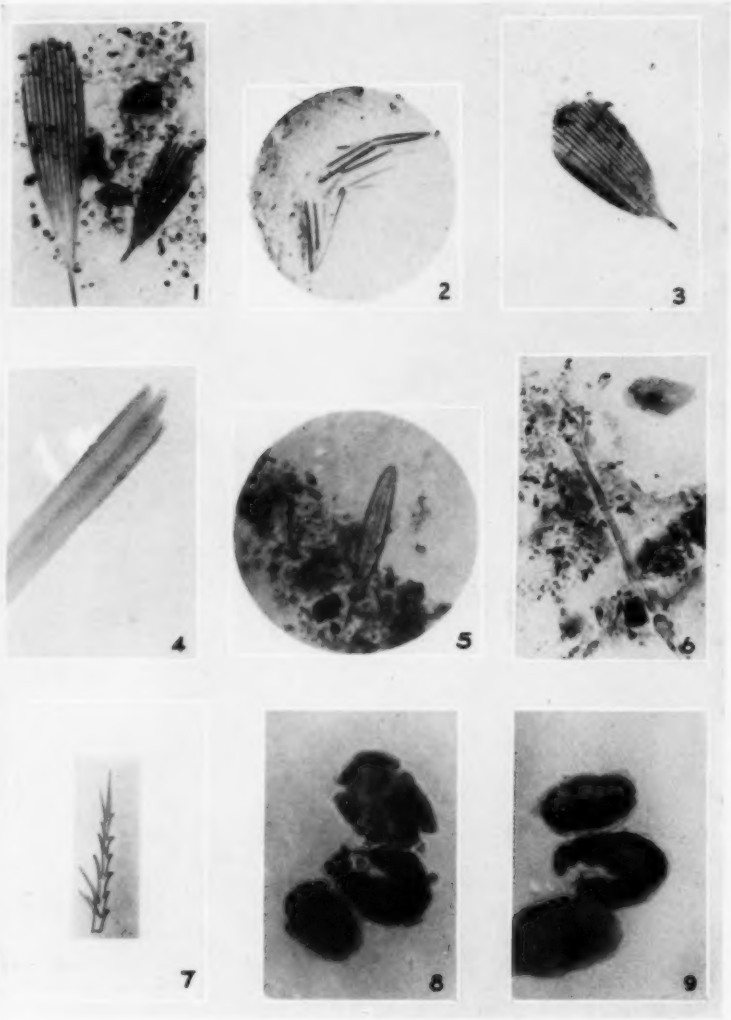
1. Unidentified object, by reflected light, Miocene oil, Teapa, Mexico. (× 460.)
2. The same by transmitted light. (× 480.)
3. Portion of same by reflected light. (× 1200.)
4. Silicified plant remains, Pliocene oil, Moreni, Roumania. (× 48.)
5. The same by reflected light. (× 50.)
6. Partly mineralized tissue, low focus, Eocene oil, Tamantao, Mexico. (× 640.)
7. The same, high focus. (× 640.)
8. Semi-silicified wood fragment, Miocene oil, Assam. (× 376.)
9. The same by polarized light. (× 376.)

PLATE V.



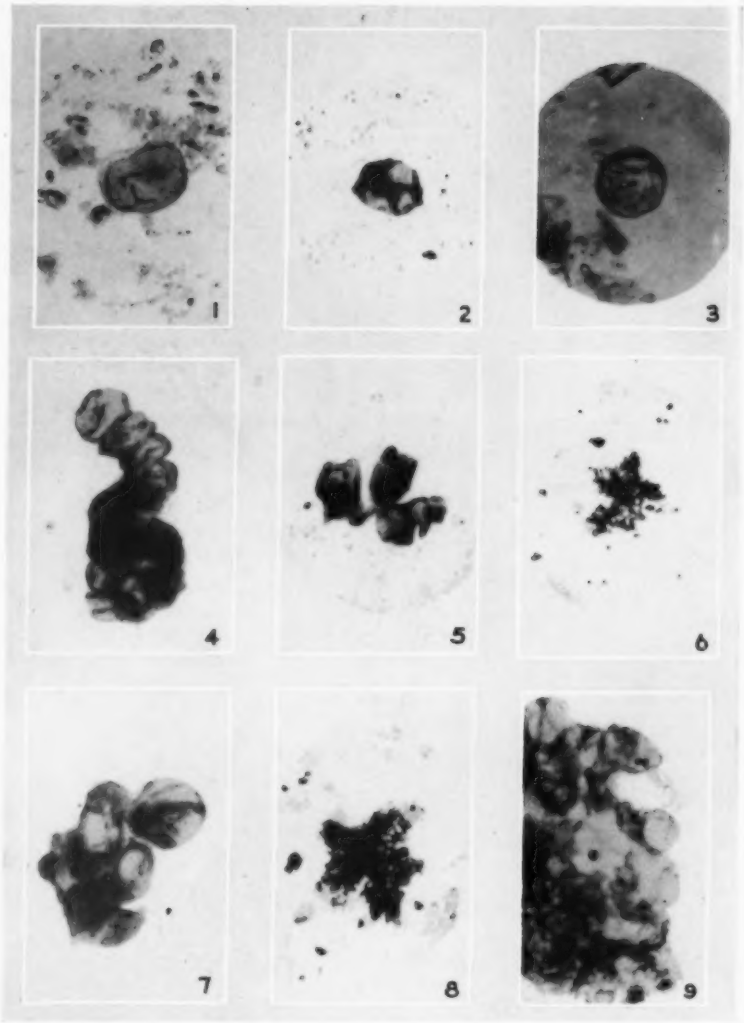

1. Silicified Cyperus fruit, Miocene oil, Assam. (× 41.)
2. Crustacean limb, Miocene oil, Sarlat, Mexico. (× 640.)
3. ,, ,, Eocene oil, Tamantao, Mexico. (× 480.)
4. ,, ,, Miocene oil, Sarlat, Mexico. (× 740.)
5. Insect remains, Miocene oil, Sarlat, Mexico. (× 167.)
6. ,, ,, Eocene oil, San Marcos, Mexico. (× 196.)
7. Acarina Sp. core from Jurassic well, San Manuel, Mexico. (× 75.)
8. The same by polarized light. (× 75.)
9. Insect appendage, Pliocene oil, Moreni, Roumania. (× 175.)

PLATE VI.



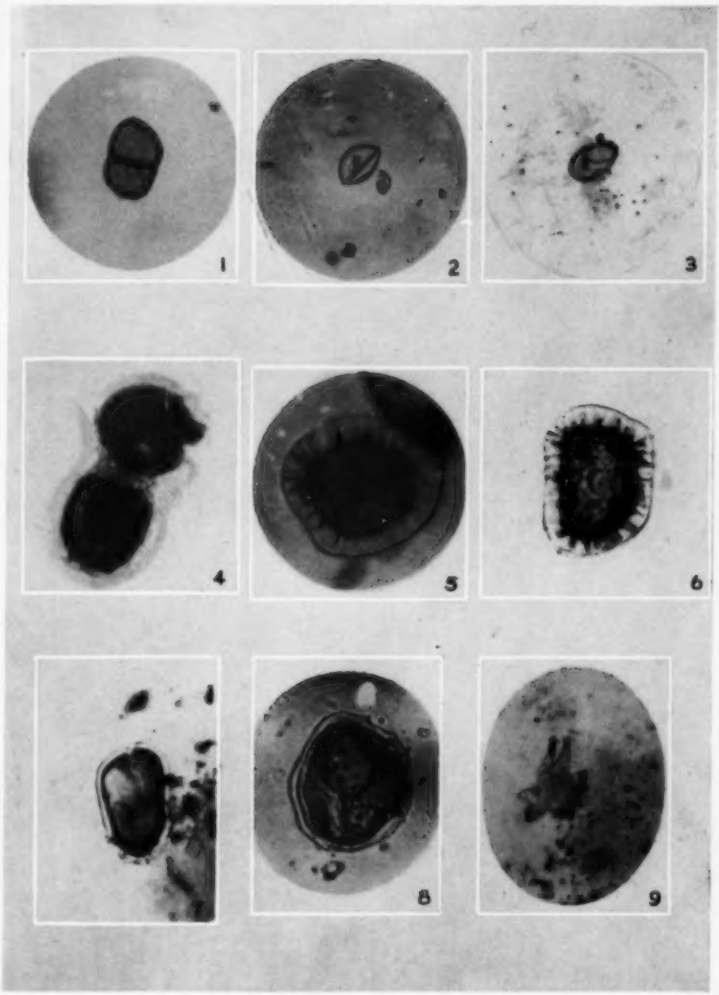

1. Insect scales, Miocene oil, Sarlat, Mexico. (× 696.)
2. Insect wing, Miocene oil, Assam. (× 20.)
3. Insect scale, Miocene oil, Sarlat, Mexico. (× 640.)
4. „ „ Miocene oil, Sarlat, Mexico. (× 640.)
5. „ „ Miocene oil, Filisola, Mexico. (× 700.)
6. Feather barbule, Miocene oil, Moreni, Roumania. (× 640.)
7. „ „ Miocene oil, Steaua Romana, Roumania. (× 640.)
8. Cellular organism, Cretaceous oil, Potrero, Mexico. (× 640.)
9. „ „ Cretaceous oil, Potrero, Mexico. (× 640.)

PLATE VII.



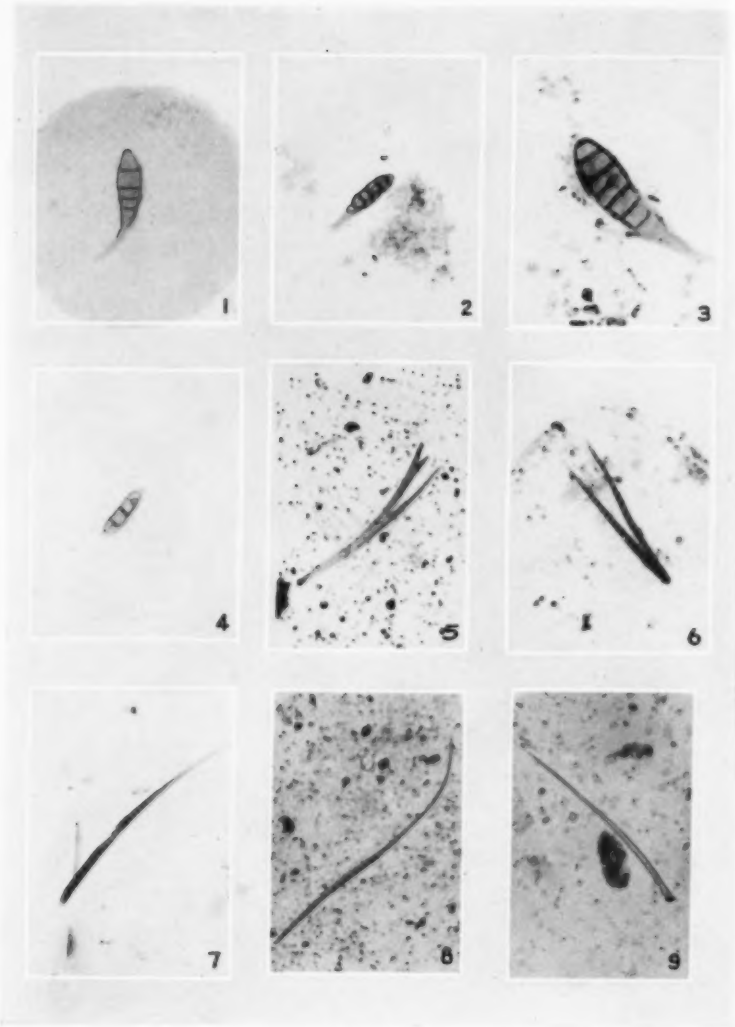

1. Spore-coat, oil from Salt Formation, Steaua Romana, Roumania. (× 640.)
2. " " " " Miocene, Moreni, Roumania. (× 640.)
3. " " " " Miocene, Filisola, Mexico. (× 750.)
4. Colonies of cellular organisms, Eocene oil, Tamantao, Mexico. (× 480.)
5. " " " " Cretaceous oil, San Diego, Mexico. (× 537.)
6. " " " " Eocene oil, Mecatepec, Mexico. (× 96.)
7. " " " " Cretaceous oil, Tamiahua, Mexico. (× 640.)
8. As No. 6. (× 120.)
9. Colony of organisms from Cretaceous oil, San Gerónimo, Mexico. (× 480.)

PLATE VIII.



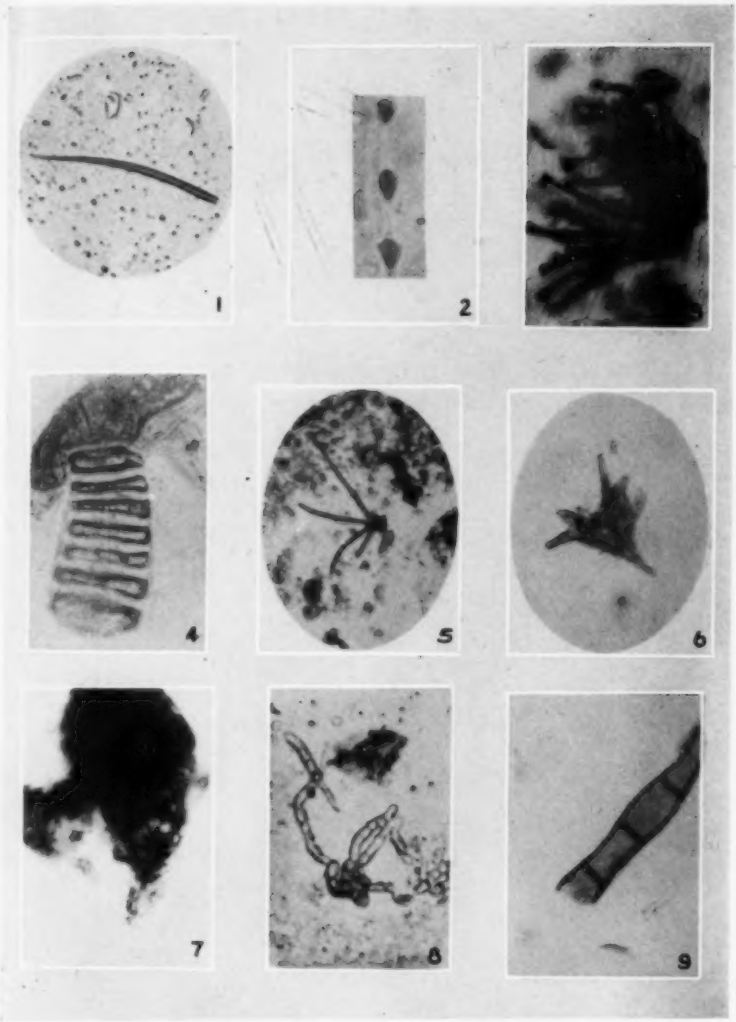

1. Bilocular spore-coat, Eocene oil, Tlacalula, Mexico. (× 640.)
2. Minute spore-coat, Eocene oil, Tlacalula, Mexico. (× 1460.)
3. Spore-coat, Eocene oil, Tamantao, Mexico. (× 516.)
4. Thick-walled cells, Cretaceous oil, Potrero, Mexico. (× 1200.)
5. „ „ „ Eocene oil, Tlacalula, Mexico. (× 1463.)
6. „ „ „ Cretaceous oil, Tamiahua, Mexico. (× 1200.)
7. „ „ „ Miocene oil, Sarlat, Mexico. (× 640.)
8. Cellular organism, Cretaceous oil, Tamiahua, Mexico. (× 1200.)
9. „ „ Salt Formation, Steaua Romana, Roumania. (× 310.)

PLATE IX.

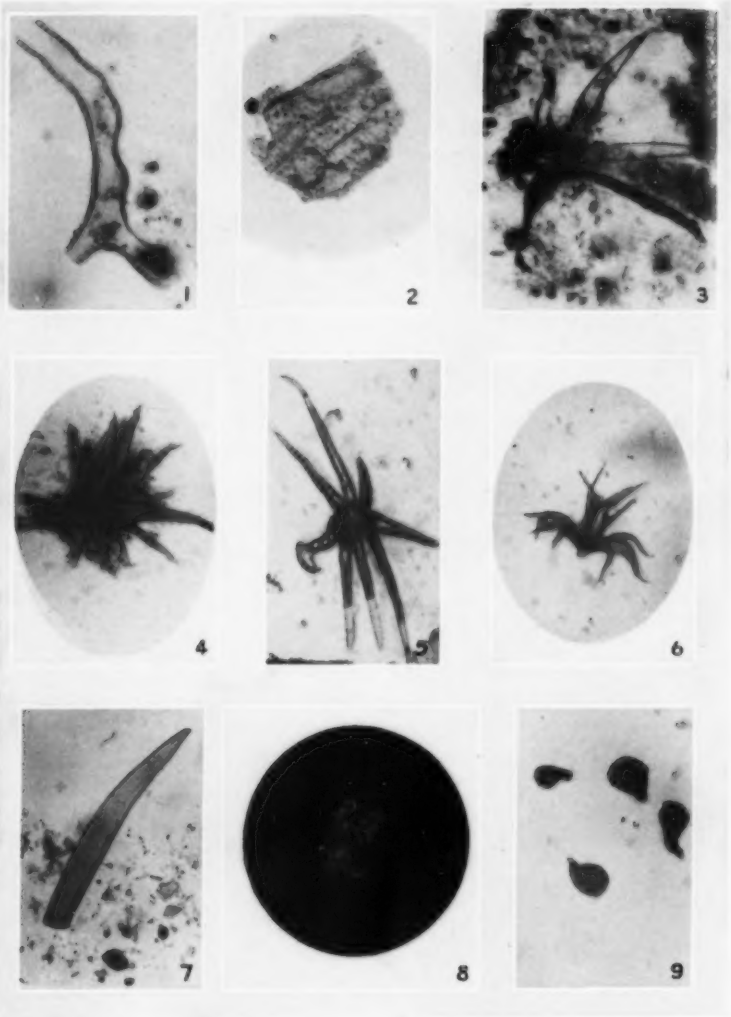



1. Antheridium, Miocene oil, Sarlat, Mexico. (× 640.)
2. ,, Eocene oil, Tlacalula, Mexico. (× 640.)
3. ,, Eocene oil, Mecatepec, Mexico. (× 1200.)
4. ,, Eocene oil, Tlacalula, Mexico. (× 640.)
5. Branched Seta, Miocene oil, Sarlat, Mexico. (× 640.)
6. ,, ,, Miocene oil, Sarlat, Mexico. (× 640.)
7. Unbranched Seta, Miocene oil, Sarlat, Mexico. (× 376.)
8. ,, ,, Miocene oil, Sarlat, Mexico. (× 640.)
9. ,, ,, Miocene oil, Moreni, Roumania. (× 376.)

PLATE X.

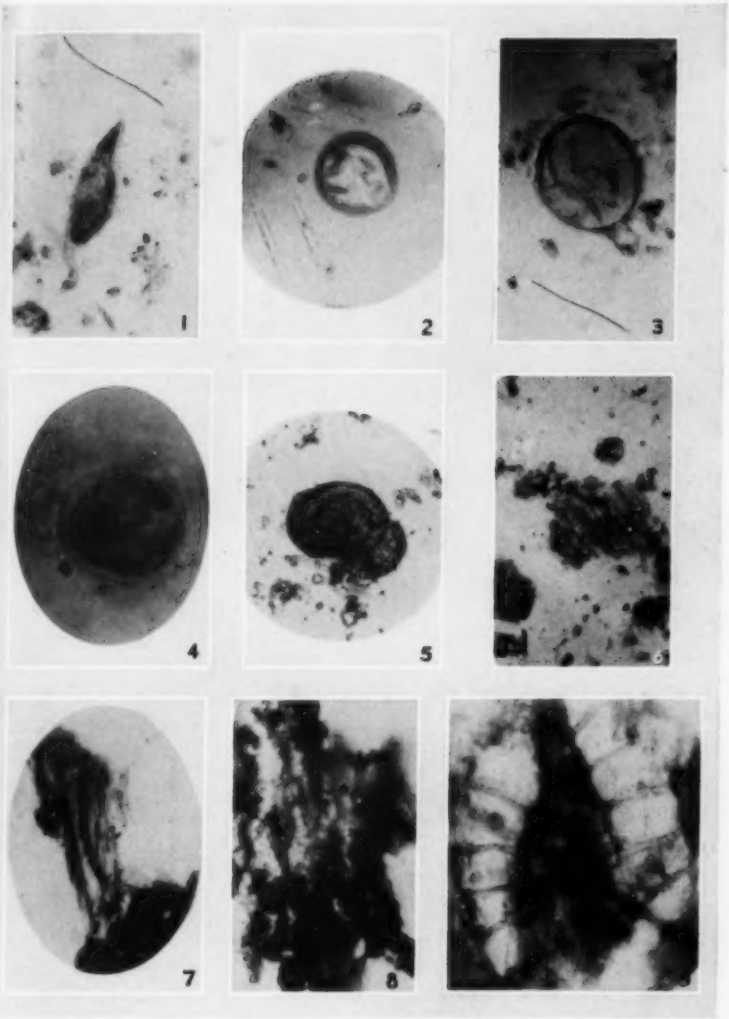



1. Seta, Miocene oil, Sarlat, Mexico. (× 640.)
2. Algal remains, Cretaceous oil, Tamiahua, Mexico. (× 640.)
3. " " Cretaceous oil, San Diego, Mexico. (× 480.)
4. " " Cretaceous oil, Tamiahua, Mexico. (× 376.)
5. " " Cretaceous oil, San Diego, Mexico. (× 120.)
6. " " Eocene oil, San Marcos, Mexico. (× 165.)
7. " " Jurassic oil, Tecuanapa, Mexico. (× 480.)
8. Fungal hyphæ, Cretaceous oil, Potrero, Mexico. (× 640.)
9. " " Miocene oil, Sarlat, Mexico. (× 1200.)



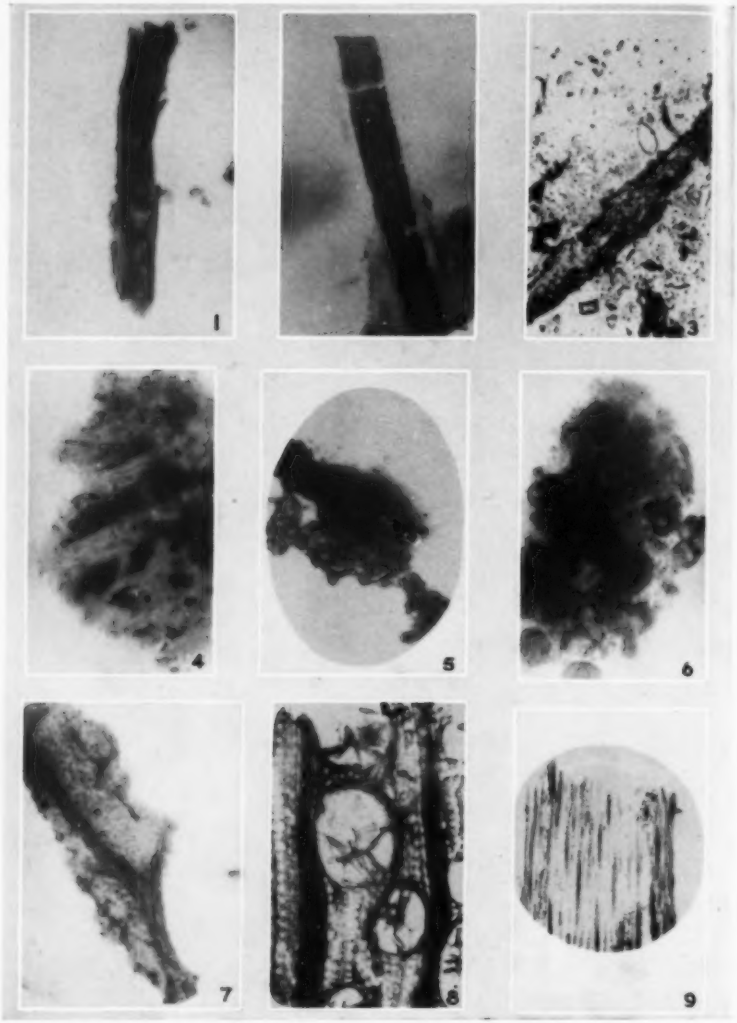

1. Fungal hypha, Cretaceous oil, Huitzalté, Mexico. (× 560.)
2. Cuticle, with parasitic organism, Cretaceous oil, Tamiahua, Mexico. (× 640.)
3. Trichome, Eocene oil, San Marcos, Mexico. (× 640.)
4. ,, Eocene oil, San Marcos, Mexico. (× 275.)
5. ,, Jurassic oil, San Manuel, Mexico. (× 250.)
6. ,, Cretaceous oil, San Diego, Mexico. (× 163.)
7. Plant hair, Miocene oil, Filisola, Mexico. (× 376.)
8. Resin droplets, by reflected light, Miocene oil, Filisola, Mexico. (× 320.)
9. ,, ,, Salt Formation, Steaua Romana, Roumania. (× 640.)

PLATE XII.

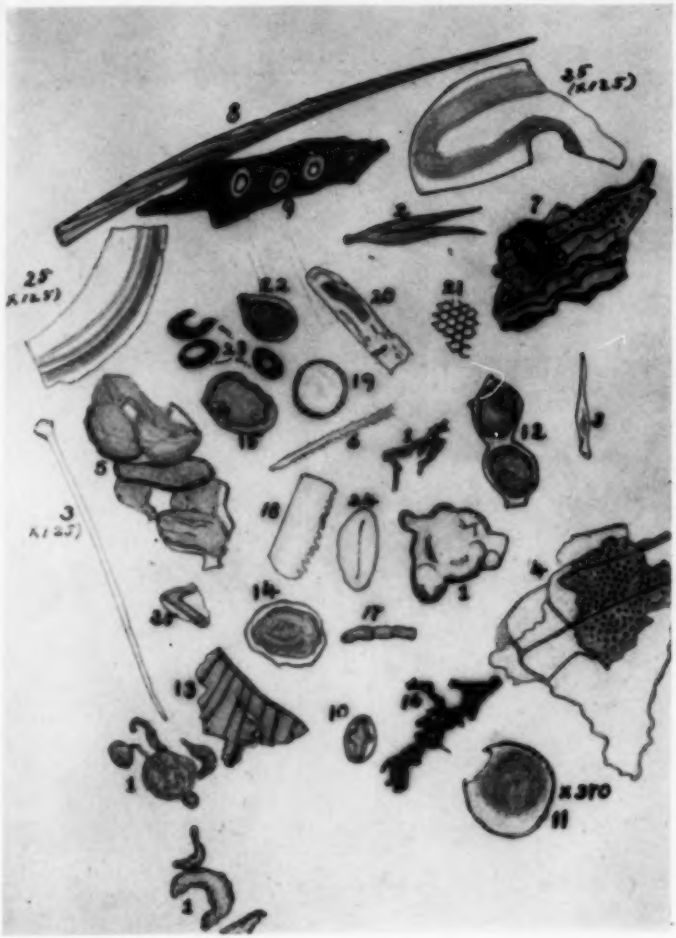



1. Unicellular organism, Salt-Formation oil, Steaua Romana, Roumania. (× 640.)
2. " " Miocene oil, Filisola, Mexico. (× 750.)
3. " " Salt-Formation oil, Steaua Romana, Roumania. (× 640.)
4. " " Cretaceous oil, Potrero, Mexico. (× 1687.)
5. Partly decomposed cellular organism, Cretaceous oil, Tamiahua, Mexico. (× 376.)
6. " " Plant tissue, Cretaceous oil, Huitzalté, Mexico. (× 120.)
7. " " " " Jurassic oil, San Manuel, Mexico. (× 158.)
8. " " " " Miocene oil, Tanhuijo, Mexico. (× 280.)
9. Part of No. 8. (× 1120.)

PLATE XIII.

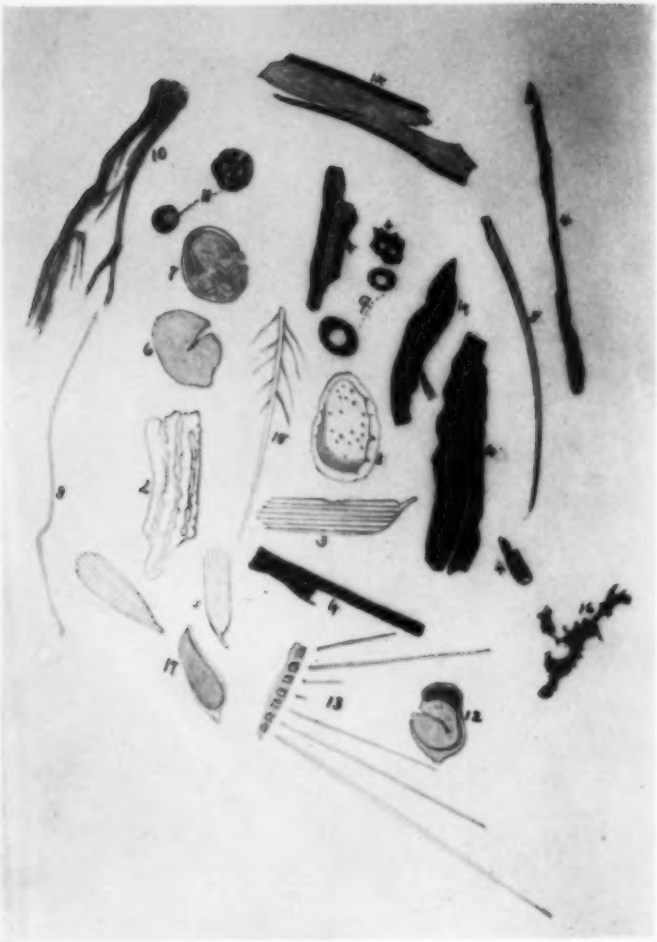


1. Partly decomposed algal thallus, Cretaceous oil, Potrero, Mexico. (× 376.)
2. " " " " Pliocene oil, Moreni, Roumania. (× 376.)
3. " " " " Miocene oil, Tonala, Mexico. (× 376.)
4. " " " " Salt Formation, St. Romana, Roumania. (× 376.)
5. " " " " Cretaceous oil, Altamira, Mexico. (× 120.)
6. " " " " Miocene oil, Sarlat, Mexico. (× 640.)
7. " " " " Pliocene oil, Moreni, Roumania. (× 88.)
8. Dipterocarpus wood, transverse section, Oil-well wax, Assam. (× 100.)
9. " " tangential section, Oil-well wax, Assam. (× 20.)




Typical micro-objects found in a Roumanian Miocene oil, Moreni field.
(All × 400 except where otherwise indicated.)

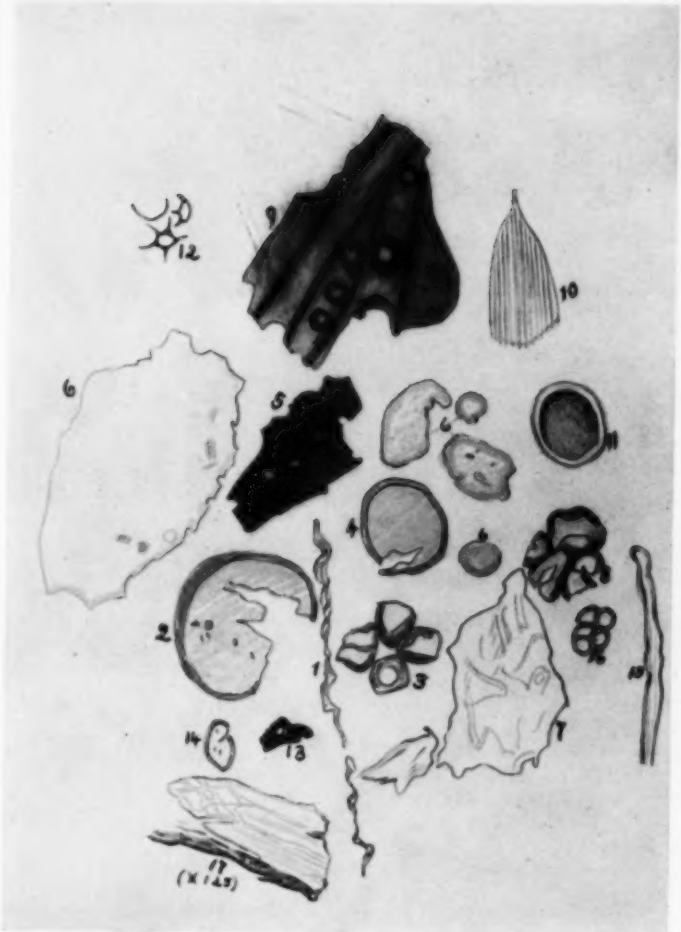
1. Resin droplets and aggregates.
2. Algal remains.
3. Plant hairs.
4. Fragment of partly decomposed vegetable tissue.
5. Pale-yellow, thin-walled cellular organisms.
6. Insect hair.
7. Partly carbonized plant tissue.
8. Siliceous spicule with spiral grooving.
9. Lignitic fragment with bordered pits.
10. Small spore exine.
11, 14, 15, 19, 22, and 24. Larger spore exines.
12. Pair of thick-walled cells.
13. Partly carbonized plant tissue.
16. Completely carbonized tissue.
17. Fragment of fungal hypha.
18 and 25. Fragments of molluscan shell.
20. Partly decomposed algal thallus.
21. Carbonized cellular tissue.
23. Black, oval bodies found adherent to lignitic fragments or detached.



Micro-objects from same oil as in Plate XIV. (All × 365.)

1. Pale yellow, thick-walled cell, perforate walls.
2. Nearly colourless fragment of epidermal tissue.
3. Insect scales.
4. Lignitic fragments.
5. Seta (Chætophorales ?).
6, 7, and 12. Spore exines.
8. Colourless filament.
9. Similar to No. 23, Plate XIV.
10. Molluscan byssus ?
11. Pyrite globules.
13. Unidentified (see text, Section VII, group 3 [*a*]).
14. Lignitic fragment.
15. Remains of leaf venation.
16. Carbonized tissue.

*Note.*—On account of the numerous particles of resin found in this oil, it was found possible to extract a portion for examination. It was found to have a saponification value of 80, and an iodine value of 46. It gave a negative reaction for colophony by the Storch-Morawski reagent, and was insoluble in cold acetic anhydride. Its solution in acetone was intensely blue-fluorescent.




Micro-objects found in a Roumanian Pliocene oil, Moreni field. (All × 370 except where otherwise indicated.)

1. Axial remains of shell.
2. Sporangium.
3, 4, 8, 11, 14 and 16. Spore exines.
5, 9 and 13. Lignitic fragments.
6. Masses of silica with traces of carbonized tissue.
7 and 17. Fragments of cuticle.
10. Insect scale.
12. Carbonized cellular tissue.
15. Fragment of fungoid hypha.

*Note.*—The smaller objects numbered " 6 " consisted of rounded masses of opaline silica on the outside surface of which were patches of cutinized membrane, suggesting that the silica had filled the lumina of a cellular body and preserved its shape.

Typical micro-objects found in a Mexican Miocene oil Sarlat field. (All × 365.)

1. Lignitic fragments.
2. Carbonized plant tissue.
3. Carbonized tissue embedded in silica.
4. Thick walled cellular organisms.
5. Spore exines.
6. Fungoid hypha.
7. Fragments of shell.
8. Siliceous spicules.
9. Insect scales.
10. Resin droplets.

## PART II.

## PRACTICAL RESULTS AND OBSERVATIONS.

Although the range of crude-oil types which have been the subject of the present investigation is far from being comprehensive, the number and variety of organized remains which have been brought to light are already very large, and many of them merit individual study.

It is not proposed to present a complete list of these objects, many of which are mere fragments, and would need to be identified as parts of some larger organism of known generic value, before their presence in certain oils could be regarded as significant.

This Part therefore will be concerned with the description of certain predominant types of material found by the author in the crude oils or cores which he has examined. Microphotographs will be used wherever possible to illustrate the descriptions, and where for any reason photographic methods could not be applied, camera lucida drawings will be used instead.

In addition, and for the benefit of other workers who might wish to follow up this type of investigation, there have been included certain observations of a general nature which may be of assistance.

The objects discoverable in crude petroleum by microscopical methods may be conveniently classified as follows :—

*A*. Mineral and recent material.
*B*. Decay-resistant organized material.
*C*. Decay-arrested organized material.

### *A*. Mineral and Recent Material.

In this group will be included usually a relatively large amount of mineral matter derived from the producing formation, a certain proportion of iron rust, mill scale or metallic steel scoured out of the well tubing by the oil-flow and the abrasive action of the mineral particles, and any foreign

matter of local and recent origin, which may have been introduced into the oil sample or its container.

In the process of separation by gravity the larger and heavier particles of mineral matter will be segregated from the organic matter and may be examined separately if desired. To the sedimentary petrologist they may be of interest as providing a sample of the formation, but their consideration is outside the scope of the present subject.

It is the writer's experience that separation by gravity is by no means absolute, and very finely divided mineral matter frequently accompanies the lighter organic matter, either adherent to it, or because it is so finely divided that it remains in suspension. This is specially noticeable with oils derived from sand formations, where the mineral particles frequently appear of nearly sub-microscopic dimensions.

To this group, completely mineralized (petrified or calcified) organized material belongs, but it is preferable to consider it under the next category.

The material referred to as " recent " refers to particles which may have been introduced into a sample of oil after it has left the well-tubing and before it reaches the analyst, in spite of all precautions taken to exclude it. The due recognition and rejection of such material from consideration as part of the true sample is of such importance that it is desirable to deal with the subject at some length.

It is the writer's experience, derived from the examination of a large number of well samples, that if the conditions for obtaining an uncontaminated sample have been faithfully observed, the type of recent material likely to be encountered is confined entirely to air- or wind-carried matter such as may be expected to be present in the dust of the locality.

Cotton fibre is ubiquitous owing to the prevalent use of cotton-waste by operatives, and other varieties of industrial fibrous material, such as hemp, linen, jute, hair, paper cellulose, and even sawdust may occasionally be discovered in a sample, but such intruders are easily and quickly recognized. It is conceivable also that spores, pollen grains, leaves and other vegetable debris might be air-carried to the spot where samples are being put into their containers, or carried by the clothing or person of the sampler himself.

On the other hand, there are a variety of considerations which are of assistance to the microscopist, if he is called upon to decide whether any organized material found in the oil is of recent or local origin.

Of paramount importance in this respect is his own experience, assisted by full information relating to the locality and surroundings of the well and the conditions under which sampling was performed. Complete data relating to the latter should be provided, therefore, with every sample.

A valuable aid in deciding doubtful cases is the relative frequency with which materials of the same type, even if of recent appearance, can be found in oils coming from different localities and with distinct environments.

Objects of marine origin, derived from wells far removed from any contact with marine conditions on the surface may legitimately be considered as belonging to the oil, to the formations from which it was produced, or to those through which it has passed during migration.

It should be borne in mind also that the organized material likely to be found in the oil may be of two types :

(*a*) Residual, decay-resistant parts of organisms which originally may have played a major part in the genesis of the oil.
(*b*) Organized material which became incorporated in the oil subsequent to the latter's birth.

Material belonging to the second category may have been simply a recent addition to a magma of decomposing organic matter in which oil was already formed, or it might have been picked up by the oil from some other source during its migration.

In the latter case, the material, if undecomposed, may have been preserved originally by some other agency such as the aseptic medium which has been postulated as the preservative agent for the organized material in coal, or peat. If partially decomposed or decomposing, the oil would either perpetuate the original preservation or arrest any further decay.

Assuming that such material became incorporated in the oil at a very early stage, that is to say, before any decomposition of the organic matter had taken place, yet it could not fail to betray eventually some evidence of its long-continued contact with the hydrocarbon oils, when examined at a much later date. The oily, waxy and often the resinous contents of cells, the waxy or resinous coatings of cuticles and spores, as well as certain pigments, would be removed or dissolved by the oil, while starch, inulin, plant crystals, raphides and other oil-insoluble matter might remain. Hence, the material would differ considerably from fresh, recently organized material which had fallen into a sample a few weeks before reaching the analyst's hands.

It should be observed, however, that apart from the solvent effect of the hydrocarbons upon the constituents or cell contents of the organized material, the latter must be presumed to have been exposed to the combined effects of temperature, pressure and time, and this may have had a profound effect upon them.

The temperature of many crude oils at depth is known to exceed that at which starch gelatinizes in the presence of water, and it might conceivably have been high enough to effect still greater changes, especially when accompanied by high pressure for long periods. Many other chemically fragile substances could be included in the category of material likely to have suffered changes through temperature and pressure conditions. It will therefore be obvious that the latter and their effects provide a means for differentiating between recent and ancient inclusions in the oil.

The presence in terrestrial vegetable remains of chloroplasts containing green chlorophyll has been taken, somewhat arbitrarily, by the writer as an indication of recent origin, and although very infrequently discovered in crude petroleums, such material has been rejected.

On the other hand, the more resistant pigment carotin, as well as the characteristic pigments in marine algæ have been accepted as legitimate accompaniments of non-recent material.

The presence of moisture or otherwise in organized tissues is of questionable value as an indication of relative age, since, on the one hand, sun or air-dried recent material is just as likely to be transported by air currents as that which retains its natural humidity, and on the other hand, crude oil is frequently accompanied by water.

It has been observed, however, that many of the preserved remains found in crude petroleum present an appearance of extreme desiccation, frequently being hard and brittle and incapable of imbibing water with facility.

Fragments of organized material which have been exposed to the conditions incident to the passage of oil through a rock formation, and subsequently subjected to high-velocity flow through the well tubing must be present in a different state of aggregation from that of recent material which has merely dropped into the oil, and this difference is frequently quite characteristic and recognizable. Such conditions are not an invariable accompaniment to oil-well samples, however, since the velocity of flow may slow down or even cease owing to the accumulation of wax, and, as in an actual example referred to later, the organized bodies may be trapped by the wax and preserved from mechanical damage.

The usual micro-chemical or staining tests are frequently of service in differentiating recent from ancient material. In the writer's experience, a positive reaction for cellulose is rarely obtainable with preserved tissue, and is never complete. Either a very faint coloration is obtained, or only a part of the tissue which should be all cellulosic, reacts as such.

On the other hand, lignified or cutinized elements react sharply unless the material is in a state of arrested but already advanced decay, in which case the material does not react at all. Such results are different from those obtainable with recent material.

The appearance of the material by polarized light is also useful for rapidly detecting recent material, since cellular structures which are in a state of arrested decay are generally isotropic unless partly or wholly mineralized. In either case they present a different appearance to that of recent origin.

Fluorescence analysis by ultra-violet irradiation may also be of service in this connection, but chiefly when direct comparison is made between the specimen and recent material of similar type.

Finally, it may be observed that core samples from the producing formation when available, provide an excellent check upon the material found in the oil.

Samples taken from the interior of a solid core may be considered to be exempt from contamination by outside sources, and if organized material is found therein which is identical with that carried by the oil, it is reasonable to conclude that a common origin may be attributed to both. Examples of such correlation will be given below when describing some of the typical forms of organized material which have been isolated and examined by the author.

### *B.* Decay-Resistant Organized Material.

The typically decay-resistant material found in crude petroleum may be conveniently divided into three main groups as follows:—

(1) *Mineralized matter*, including the siliceous or calcified skeletal frameworks or tests of organsims and petrified remains generally.

(2) *Semi-mineralized matter*, comprising those examples of preserved organized material in which the organic substance has not been entirely

replaced by mineral matter.* It thus includes incrustations as usually understood, but also comprises a form of preservation which appears to be peculiar to the present subject; a species of arrested petrification in fact.

To account for the examples discovered during the investigation, the writer suggests that in the preliminary stages of silicification due to the immersion of the organism in a liquid containing alkaline silicates in solution, silica will be deposited first in a gelatinous form upon those parts which are acid. This acidity may be a normal secretion of the organism or be the result of its bio-chemical decomposition.

The subsequent conversion of gelatinous silica into a hard matrix or petrification would only be accomplished after the lapse of time, during which natural agencies such as dehydration and pressure played their part in consolidating the siliceous coating.

Under the conditions postulated by McKenzie Taylor [25] for anærobic decomposition in an alkaline environment through base-exchange, the organic substance might be partially or entirely dissipated, but it is possible that at some intermediate stage between the deposition of gelatinous silica and its consolidation into a hard matrix the organism might be enveloped in oil so as to arrest the consolidation process as well as that of decay.

This would account for the presence in petroleum of preserved organisms which are partly mineralized, and yet which also have some of their organic texture remarkably well preserved.

Even in the case of organisms which acquired a mineral coating during life, such as the lime-encrusted siphonales and charales, their impregnation with oil might preserve some of their organic substance, and thus they might differ from the mere shells of lime which characterize the well-known type of fossil.

It may be remarked that no examples of this latter class have definitely been identified in the oils so far examined, although the specimen referred to and illustrated in Plate IV (Nos. 6 and 7) may belong to this type of calcareous alga.

In the specimens which were partly silicified the organic matter has shown considerable diversity as regards its state of preservation. In some cases black and semi-carbonized and almost devoid of structure, in others bleached and with cellular tissue almost intact.

It has also been observed that frequently there exists in the same oil parts of the same type of organism, but in different states of preservation, a fact which is not incompatible with the general theory that the process of arrestment might take place at any stage after the inclusion of the organism in a sedimentary deposit, or even before this happened if circumstances were favourable.

(3) *Non-mineralized matter*, which comprises those organisms, or parts of them, which owe their survival to their inherent resistance to the agencies of biochemical decomposition. This type of preservation is also found in

* It is recorded by Stopes and Wheeler (*loc. cit.*, pp. 20–21) that the hard, stony matrix of a specimen of petrified plant was dissolved in a mixture of hydrofluoric acid and alcohol, leaving the whole of the plant tissue in a state which could be stained, like living tissue, with saffranin. These authors conclude that replacement of cell-wall molecules atom by atom with silica need not necessarily take place as an accompaniment of petrification, a view which is endorsed by the present writer.

coal, lignite and oil-shales, but in the case of the oil-preserved material the deformation produced by pressure and compaction may be absent. On the other hand, except with the smaller types of organized material, external damage may have taken place during the passage of the oil through a formation or by attrition during its flow through the well tubing.

Some examples and observations relating to the three groups above mentioned are given below.

## *GROUP* 1. *MINERALIZED MATERIAL.*

### *Foraminifera.*

The fragmentary remains of foraminiferal tests have been found in nearly all the oils so far examined. Examples of vitreous, porcelaneous and arenaceous types were represented, usually in the form of detached chambers, or pieces of sculptured or perforated walls. The question whether such fragments could be identified as parts of known fauna is one which only an expert foraminologist could decide, and little attention has been given to them in the present investigation.

Occasionally what looked like complete tests of these animals were found. These were very small (about 25 microns in diameter) spherical bodies, lead grey in colour with irregular white patches of strongly adherent silica. In one case a sigmoidal vent was observed.

In a core taken from 10 feet above the producing formation of a well which tapped a lower miocene sand in Mexico, a foram was found which was brick-red in colour with glistening specks of pyrite and a highly polished, smooth surface. The test appeared to be built up of minute grains of sand and pyrite, it is illustrated in Plate I, No. 1, and it was also observed that the oil from this same well contained fragments of apparently the same animal, only white and porcelaneous instead of red. The oil also contained several examples of the little grey tests mentioned above.

### *Pyrite Globules.*

These minute concretions were found in nearly all the crude oils. They were specially numerous in asphaltic and mixed-base oils of high sulphur-content. That their presence is intimately associated with the action of sulphate-reducing bacteria can scarcely be doubted, but it is not yet clear whether they represent merely a spheroidal form of iron sulphide or the pyritized colonies themselves.

It has been observed, however, that they are frequently found adherent to the partly decomposed remains of vegetable matter. An example of this is shown in the microphotograph, Plate I, No. 2, where several of the globules are partly embedded in the substance of a vegetable cell, which has a deposit of mineral matter (probably gypsum) inside it.

The diameter of the globules varies from 2 to 25 microns, with an average of approximately 8 microns, and in colour they vary from brass-yellow with a brilliant metallic lustre to a reddish-yellow with occasional patches of white silica. In many cases the surface is covered with minute protuberances suggesting an aggregation of small spheres, and on crushing these between glass plates still smaller spheres can be seen detaching them-

selves from the outer periphery of the radial segments into which they break.

Owing to their small size and brilliant lustre, good microphotographs of these particles were unobtainable, but camera lucida drawings are shown in Plate XV, No. 11.

*Diatoms.*

The siliceous frustules of the *bacillariophyceæ* are of frequent occurrence in oils, and so far as the present investigation has proceeded, are chiefly noticeable in oils of relatively high nickel-content.

Representatives of both centrales and pennales were found, with the former predominating in frequency and always of the discoid type. Identification of various species was not always possible owing to the frequent accompaniment of extraneous matter and a great deal of fragmentation, but representatives of the following genera appeared to be present:

Centrales: *Actinoptychus, melosira, coscinodiscus, stephanodiscus, cyclotella.*
Pennales: *Synedra, eunotia, navicula, cymbella, maphora.*

Illustrations of some of the less injured or obscured specimens are given in Plate I, Nos. 3 to 9, and Plate II, Nos. 1 to 6.

*Radiolaria.*

The skeletal remains of these protozoans were only found in a much fragmented condition and only in the oils which carried diatoms.

Identification was not attempted, although possibly this could be done by a specialist in the subject. One specimen (Plate III, No. 1) was peculiar in that its framework appeared to have been originally of a horny, non-rigid type, although as found it was rigid but compressed and contorted.

Illustrations of some representative fragments are shown in Plates II, Nos. 7 to 9, and III, Nos. 1 to 4.

*Siliceous Spicules.*

These were found in fair profusion in cretaceous and miocene oils, both Mexican and Roumanian. The predominant form was that of very slender, straight, colourless rods, with broken extremities at right angles to the axial direction. Their diameters ranged from 1 to 2 microns and they appeared to taper very slightly or not at all. In addition there were found a few short rods of large diameter with no axial indications, some undoubted sponge spicules and some other forms which are illustrated in Plate XIV, No. 8, and Plate XVII, No. 8.

It is remarkable that no calcareous spicules were found in any of the oils examined, so that if the slender spines mentioned above belonged to genera of the foraminifera, globigerina or orbulina, the calcareous matrix must have been replaced by silica.

*Shells.*

Molluscan remains were found in several cretaceous and miocene oils from Mexico, but more frequently in those from the miocene in Roumania.

Although too much fragmented for identification, some of the remains occasionally presented features of interest.

The specimen shown in Plate XVI, No. 1, appeared to be the axial part of a shell from which the greater part has been eroded away. It was quite structureless and silicified, its calcium content having been replaced.

Other fragments are shown in Plates XIV, No. 25, XVII, Nos. 7, 7, and one in particular (No. 25) is representative of many similar specimens which showed large circular, or ovoid, perforations, larger on one side of the lamina than on the other, and suggesting that they were the work of perforating algæ of the *Gomontieæ*. Careful search of the oil samples carrying these remains, however, failed to discover any vestiges of the destructive organism. None of these specimens had any prismatic or nacreous structure.

*Petrified Wood and Encrustations.*

Completely mineralized vegetable remains have been found only occasionally in the oils so far examined, and usually in very small fragments in which the structure has been somewhat ill-defined. Microphotograph No. 5 (Plate III) shows a typical fragment which was dark-brown in colour but sufficiently translucent to show a cellular texture in one place.

Other specimens, all silicified, are shown in Plate III, Nos. 6, 7 and 8, the first being taken by polarized light only, the two latter by transmitted and polarized light respectively.

In Plate IV (Nos. 1, 2 and 3) are shown various aspects of a curious silicified object at present unidentified. No. 1 shows the appearance by dark-ground illumination and No. 2 by transmitted light, while the greatly magnified portion (No. 3) shows that each little dot in the other aspects is a tiny cone or protuberance.

## *GROUP 2. SEMI-MINERALIZED MATERIAL.*

The example already referred to (Plate I, No. 2) showing the pyrite globules, is also representative of material partly mineralized, but still possessing some of its original organic structure. The cell-wall was stained brown by chlorozinc iodide. The white mineralized portion was slightly soluble in hot hydrochloric acid, and gave positive microchemical reactions for calcium and sulphate.

In microphotographs 4 and 5 (Plate IV) are shown the appearance by transmitted and reflected light, respectively, of two vegetable organisms which were encrusted with silica, the organic substance in this case being black and carbonized with very little structure left.

An interesting specimen of a partly mineralized organism is shown in microphotographs Nos. 6 and 7 (Plate IV). No. 6 shows the appearance with low focus, the yellow-brown surface having a well-defined hexagonal cell structure. On raising the focus each cell appears to be traversed by dark lines, which are due to minute, slightly conical pegs of calcite which behave like cylindrical lenses. One of these cones can be seen projecting from the edge of the structure about midway along the right-hand side in photograph No. 6. Under polarized light the projections are seen to be anisotropic with straight extinction.

The fragment was slightly curved and elastic, as shown by its yielding to pressure on the cover-glass. The organic material was stained brown by chlorozinc iodide.

The object has not been identified and has been found in only two oils, both producing from a formation of eocene age.

In a sample of oil-well wax from Assam there were found numerous fragments of semi-silicified dipterocarpus wood, as well as some completely petrified, and a few in which apparently no silicification had taken place at all, since, although hard and friable when removed from the oil, they could be softened by treatment with potash, and sections cut with comparative ease. The semi-petrified pieces could not be so dealt with on account of their brittle, friable nature, but by infiltration with synthetic resin it was possible to prepare a thin section, of which microphotograph No. 8 (Plate IV) is a reproduction. The woody portion gave a faint reaction for lignin, and as shown in photograph No. 9, the encrusting silica is evidenced by the appearance with polarized light.

In this same sample were found two small cyperus fruits almost entirely silicified and coated externally with a siliceous sinter. On removal of the latter the silicified fruit was seen to have its external form remarkably well preserved, as shown in microphotograph No. 1 (Plate V). The main bulk of the specimen was soluble in hydrofluoric acid, leaving only a few fragments of cell-walls and fibres which gave no reaction for cellulose but a faint one for lignin.

In drawing No. 3 (Plate XVII) is shown a mass of semi-carbonized vegetable tissue embedded in a mass of siliceous material, similar to that which encrusts the specimens shown in Plate IV (Nos. 4 and 5) contained in the same oil.

### *GROUP 3. NON-MINERALIZED, DECAY-RESISTANT MATERIAL.*

This group may be conveniently sub-divided into (*a*) fauna, and (*b*) flora, and it includes a variety of inherently decay-resistant organic material which not infrequently is found preserved in sedimentary deposits, coal and lignities as well as in petroleum.

#### (a) *FAUNA.*

The chitinous integuments of small crustaceans have been found in a number of oils, and also the detached limbs or appendages of terrestrial insects.

As found in the oils, these remains were invariably colourless and devoid of any discernible internal structure, as will be observed in the microphotographs (Plate V, Nos. 2 to 6), especially Nos. 2, 3, and 4 which are highly magnified, and No. 5 which shows the crumpled vestiges of the whole organism as a mere film or ghost of its original form.

An example of more perfect preservation is shown in the specimen of acarina illustrated in Nos. 7 and 8 (Plate V). This was found in the interior of a core taken from a jurassic shale which is presumed to be the mother-formation of the cretaceous oils in Mexico. As will be seen in the photograph (No. 8) taken by polarized light, the body of the insect is encrusted

with little crystals of calcite and its spinous processes are apparently completely mineralized. The apparent internal structure is outlined by black carbonaceous matter.

*Insect Scales.*—As already mentioned, these chitinous appendages have been found in many crude oils, as well as in core samples. Examples are given in microphotographs Nos. 1 to 5 (Plate IV) and drawings No. 3 (Plate XV), No. 10 (Plate XVI, and No. 9 (Plate XVII).

A curious object, believed to be part of an animal organism, is shown in the drawing No. 13 (Plate XV). The long, slender hairs are sheathed at their roots in a kind of follicle, and under a high magnification each one was found to possess a medula extending nearly the whole length and filled with a black granular substance. One or two fragments of insect hairs were found in the oils which carried scales, and in photograph No. 9 (Plate V) is shown what is thought to be the appendage of some insect. Plate XIV, No. 6, shows another.

*Feather Barbules.*—Owing to the absence of colour and extreme tenuity of these remains it was difficult to secure good microphotographs. Two types are shown, however, in Plate VI, Nos. 6 and 7.

(b) *FLORA.*

It may be of significance that representatives of the vegetable kingdom far exceed in number and frequency of occurrence the animal remains found in crude petroleums, and it is remarkable also that the former are of similar character to those found in lignites and coals, although not often identical with them.

*Spore-coats and Unicellular Organisms.*

These appear to be ubiquitous and they are so conspicuous among the many micro-objects carried by crude petroleum that they are worthy of more detailed study than has been given them in this investigation.

They have been found in great variety as regards shape, dimensions and colour, and while the majority are of the decay-resistant type, quite a number of specimens have been found which still retained vestiges of unaltered cellulose and a few which gave a reaction for starch, although actual starch grains were not found in them, and were scarcely expected to have survived sub-surface conditions even when immersed in oil.

Only those cellular bodies which were represented by the hard and cutinized outer coats or exines have been included in this section, those which appeared to have still retained some traces of cell-contents being classed as "decay-arrested." In a few cases the walls appeared to be silica-bearing and resemble the coccoid forms of the *Xanthophyceæ*. A general description is difficult owing to the great variety of specimens encountered in the different oils, in fact it appears probable that with more extensive investigation it may be possible to characterize certain types of oil by their spore or cell-contents. In shape the cellular organisms varied from nearly spherical to narrow pyriform, ovate, ovoid or obovate. In the majority of examples the walls were thin and apparently hard and brittle, since they frequently presented a broken appearance as shown in microphotographs Nos. 8 and 9 (Plate VI), drawings Nos. 6, 7 and 12 (Plate

XV), and Nos. 2, 4 and 14 (Plate XVI). In size, also, there is considerable variation. The largest ovoid form discovered measured 75 × 60 microns, the smallest 21 × 14 microns. Among the nearly spherical forms the largest measured 43 and the smallest 7 microns in diameter.

The colour varies from olive-brown to very pale yellow, with intermediate shades of yellow-brown, grey-brown, orange and yellow. In those found in the cretaceous and miocene Mexican oils the predominant colour was yellowish-brown. In the Roumanian oils which carried a plentiful assortment of terrestrial debris, the colour was chiefly yellow or nearly colourless, whereas an oil from the salt-formation in Roumania carried brown-coloured specimens.

Generally speaking, these remains were mere empty sacs devoid of protoplasm, nuclei, chloroplasts or other cell-contents, consequently their identification would appear to be difficult. A triradiate marking was occasionally noticed, as shown in Plate VII (No. 1), and a few very small tetrads were found in a Mexican miocene oil (Plate XVII, No. 5). A light-yellow cell with a curious four-armed thickening on the outer wall is shown in Plate VII, No. 2.

Usually the outer surface was smooth and free from sculpturing or distinctive markings, but the effect of desiccation was frequently evidenced by wrinkling, as shown in Plate VII, No. 3.

Colonies or clumps of cells were frequently observed and are illustrated in Plate VII, Nos. 4 to 9. The last example, from a Mexican cretaceous oil, is of interest in that it appeared to be in process of decomposition, being soft and almost gelatinous in consistence, the peripheral cells being nearly colourless.

The small bilocular object shown in Plate VIII (No. 1) is very like the spore of a fungus belonging to the *Puccinia*, except that it lacks the peduncle. There is, however, a gap in the lower part where this might have been originally attached. No. 2 in the same plate is also thought to be from a fungus.

The cell shown in No. 3 (Plate VIII) differed from the other examples carried by the same oil in being filled with a white mineral deposit.

The next three specimens (Nos. 4 to 6, Plate XIII) are shown highly magnified and are interesting on account of the great thickness of cell-wall, which, however, did not react for starch or similar reserve material; the outer coat was cutinized. As shown in No. 4 and partly in No. 5, these objects occurred in pairs of cells joined together, and similar pairs were frequently encountered in oils differing widely in origin.

Nos. 7, 8 and 9 (Plate VIII) show other varieties of cellular bodies, the last illustrates a pair of curious sac-like bodies, of which several single examples were also found in the same oils. They appeared to be quite structureless and have not been identified.

The olive-brown multicellular bodies illustrated in Plate IX (Nos. 1 to 4) are somewhat similar to antheridal organs of the *Phæophyceæ*, but are much smaller than, for instance, the gametangia of living species of ectocarpus, to which No. 2 bears some resemblance. They were found in eocene and miocene oils only, and no cell-contents were observed in any of the examples, which varied in length from 19 to 36 microns, with an average of 30. It is thought possible that they represent a lichen, since they were invariably accompanied by remains of fungi and algæ.

*Algæ.*

Fragments of algal thalli were found in all the cretaceous, eocene and miocene oils, and usually they were characterized by a brown or olive-brown colour. Chloroplasts were absent from the cells, and although some of the colour might be attributed to the adsorbtion of bituminous matter from the oil, and failure to remove it by prolonged washing with carbon bisulphide, the shade was remarkably uniform suggesting that it was inherent in the tissue.

The examples shown are only a section from among a great number of interesting objects of this type.

Microphotographs Nos. 5 to 9 (Plate IX) and 1 (Plate X) show various forms of setæ, which were considered to be derived from members of the *chætosphæridiaceæ*, a view which was strengthened by the discovery in some of the oils of pieces of filament consisting of nearly spherical cells united by apparently empty tubes. One of these fragments is shown in Plate X, No. 2, and although none of the cells was found to have ruptured walls or the conical sheaths of chætosphæridium, this may be due to the fact that development was arrested before maturity. Similar setæ were found in a Roumanian oil from the miocene (Plate XV, No. 5).

Other fragments of brown algal remains are shown in Plate X, Nos. 2 to 7, of which the last is specially interesting in that winding through the mass of brown tissue were septate hyphæ of a fungus-like character.

*Fungi.*

Fragments of fungal hyphæ were of common occurrence, both septate and non-septate forms being found. They were either brown or colourless, no intermediate shades were observed. Examples are shown in Plate X, Nos. 8 and 9 (the latter highly magnified) and Plate XI, No. 1.

*Cuticles and Trichomes.*

As in the case of bituminous coals, fragments of cuticle are of frequent occurrence in crude petroleum, although usually of very delicate texture and nearly devoid of colour. Examples are shown in drawings Nos. 7 and 17 (Plate XVI) and microphotograph No. 2 (Plate XI), the latter showing the cellular texture of the epidermis and the traces of attack by a parasitic organism.

Trichomes and plant hairs are also found in great variety of form, and examples from several different oils are shown in Plate XI (Nos. 3 to 7).

*Resins.*

Droplets of resinous matter were found in several oils, of Mexican, Roumanian and Indian origin. The fragments have invariably been small (about 20–25 microns in their largest dimension), pale yellow or amber-coloured, translucent and isotropic. In shape they were very irregular, but always with well-rounded contours, sometimes suggesting that they represented the form of the original cells which contained them in the living plant, at others that they had been subjected to heat or pressure sufficient to distort them.

It is significant that when found they were always accompanied by frag-

ments of lignite or carbonized wood. In some instances it has been possible to extract the resins from the oil in sufficient quantity to determine a few of their physical and chemical constants, and in one instance to identify the resin from its likeness to resin derived from a living species of plant, similar to that of which preserved remains were found in the oil.

These extracted resins gave a brilliant blue fluorescence with ultra-violet light, and the oils from which they were derived were also fluorescent.

It was further observed that in the case of two oils, one from the lower miocene in Mexico, the other from the dacic (Pliocene) in Roumania, similar resin fragments were found, and also similar types of insect scales.

Examples of these resin fragments are shown in microphotographs Nos. 8 and 9 (Plate XI), drawings Nos. 1, 1 (Plate XIV), and Nos. 10, 10, 10 (Plate XVII).

*Coal and Lignite Remains.*

Insofar as the present investigations have been carried there is little conclusive evidence that coal, in the strict sense, is a component of crude petroleum. In the case of a jurassic Mexican oil, some dense, hard, black and lustrous fragments were found by careful microscopic examination to be a species of coke, showing a minutely vesicular structure, and with no vestige of organized texture. They were thought to be the result of igneous intrusive action on some already carbonized material.

On the other hand, in some oils from the miocene in Mexico, and specially prominent in oils from the meotic and dacic in Roumania, there were plentiful examples of sharp-angled splintery fragments, which by reflected light were lustrous and jet-like, occasionally with a ribbed or corrugated appearance. Although usually opaque, there were always to be found thin translucent portions between the ribs, grey in colour and either finely perforated or showing single rows of bordered pits, as in coniferous wood. Some examples of these fragments are shown in drawings Nos. 7 and 9 (Plate XIV), 4 and 14 (Plate XV), 5 and 9 (Plate XVI), and 1 and 2 (Plate XVII).

An interesting feature, frequently observed in these remains, is the presence of small, flat, oval bodies with oval perforations which sometimes appeared to be adherent to the lignitic fragments, while at others they were detached and sometimes appeared in halves which could be found in different parts of the microscopic preparation. Examples are shown in Plate XIV (Nos. 7 and 23) and Plate VI (No. 9).

Carbonized plant tissue in a great variety of forms was found in many of the oils examined and appeared to indicate a further stage in decomposition of organized material which in the same oils was found in a state of arrested decay. Examples are shown in Plate XIV (No. 16), Plate XV (No. 16), Plate XVI (No. 12), and Plate XVII (No. 2). No. 3 in the last-mentioned plate has already been referred to as an example of semi-mineralized material.

### *C.* Decay-Arrested Organized Material.

In this group are included a few examples of what appears to constitute a new form of preservation, and to be peculiar to petroleum oil. The question whether the preserved material represents part or all of the mother-

substance of petroleum in a state of transition cannot yet be answered, but it seems probable that many of the fragments represent the residues of matter which had already contributed some part of its components to what eventually became oil. In fact proof that this has taken place in some instances is already available, as evidenced, for instance, by the discovery of a dammar-like resin in an oil from Assam and the finding of fragments of dipterocarpus wood in various states of decomposition in the same oil.

It is not proposed to deal at any great length with this side of the question, because it is precisely here that a need for further research is indicated, and the present record can only be regarded as an initial step towards securing still better and more conclusive evidence.

In the examples referred to below it will be observed that whereas some of them, as in the previous group, contain elements inherently resistant to decay, they also contain some vestiges of matter which is not specially resistant to biochemical decomposition.

In microphotographs Nos. 1 to 3 (Plate XII) are shown some spore-like objects, which, although devoid of specialized cell-contents, gave a slight but quite definite reaction for cellulose in a narrow zone on the inner periphery of the wall. The thicker-walled cell shown in No. 4, which is very highly magnified, also gave a cellulose reaction, and in addition appears to have still retained vestiges of cell-contents.

The much larger object shown in No. 5 appeared to consist of a large spherical cell, 58 microns in diameter, attached or adherent to two others. The outer surfaces of all three appeared to be in a state of incipient disintegration, but below the shredded fragments a faint reaction was again obtained for cellulose.

Microphotographs Nos. 6 to 9 (Plate XII) show examples of partial decomposition, in which, additional to the lignified elements, apparently holding the structure together, there were shreds of carbonized tissue pointing to prior partial decay. In these examples no cellulose was shown by chemical tests.

In Plate XIII (Nos. 1 to 5) are shown examples of brown algal thalli partly decomposed, but still showing vestiges of structure, the last three being almost in a state of jelly, in places where little colour was apparent. Only in the case of No. 2 was a reaction obtained, the colourless walls giving a greenish-blue coloration with Schultz's reagent.

No. 7 was also apparently a fragment of thallus, the soft tissue of which was in process of decay, since it had a vesicular appearance and was easily disintegrated by slight friction.

Nos. 8 and 9 show longitudinal and tangential sections made from a small fragment of the dipterocarpus wood mentioned previously.

These were interesting in that treatment with potash (which was applied to soften them previous to sectioning) extracted a considerable amount of red colouring-matter (this also stained the section) which had a brilliant green fluorescence. Neutralisation of the alkaline solution precipitated the pigment in flocs, which were insoluble in ether, but soluble in chloroform and hot alcohol.

Drawing No. 10 (Plate XV) shows one of several fragments of pale yellow, fibrous organic material which was found in all those oils which carried molluscan remains. The material was isotropic and structureless, with a

silky sheen by reflected light, the wider portions being flat and ribbon-like, the frayed part breaking up into filaments approximately 1·5 microns in diameter.

It was non-reactive towards reagents for plant tissues and was thought to be probably the triturated remains of molluscan byssus.

Not illustrated among the above, but considered to be of probable significance and worthy of further study, are the fragments of structureless material which were found in nearly all the oils so far examined. This material was either brown, pale yellow or colourless, and apparently amorphous, being found usually as shapeless lumps or broken into irregular flattened pieces, similar to the appearance of a jelly when pressed between glass plates.

It is thought that this material represents the equivalent of the " ulmic or humic binder " which has been mentioned by several writers as a conspicuous component of oil shales or source rocks. If in fact this material represents a further stage in the decomposition of organic matter, the penultimate one perhaps, it would be of interest to discover the final stage in which this jelly-like matter either passed into oil or was resolved into gaseous products.

In a few instances there were found fragments of structureless material, very pale yellow in colour and thickly speckled with dark-brown rodlets of uniform dimensions and with rounded ends. These were thought to be examples of bacterial attack, but were not further investigated.

## Summary and Deductions.

Although the results and observations recorded in the previous section can only be regarded as of a preliminary and exploratory nature, it will be apparent that there is sufficient material to justify further investigation along certain definite lines.

Taking first the question of the genesis of petroleum, there is evidence pointing to the extreme probability that spores and unicellular algæ have contributed their waxy, fatty, resinous or oily secretions to the eventual petroleum complex, leaving only their decay-resistant integuments behind.

The presence of oil, usually strongly coloured by yellow, red or orange pigments, in unicellular algæ is well known, and it cannot be entirely without significance that many of these have a habitat which would facilitate their inclusion in the sedimentary magma wherein the liberation of their oil contents could take place.

According to Fritsch,[26] the resting-stages in the life cycle of certain algæ is represented by spores whose cell-contents become laden with food reserves and frequently harbour quantities of yellowish-red oil. Bristol [27] shows that they are able to withstand long periods of drying and retain their vitality for a long time.

Some of the forms of unicellular organisms found in oil may be representative of these oil-secreting algal bodies, and their identification as such would be of great interest. Thus, No. 11 (Plate XIV) resembles the macrogametes of the chætophoral *aphanochæte*, which has a large and prominent oil gobule, and, as has been pointed out previously, the presence in several oils of setæ and hairs might strengthen the hypothesis that this order of algæ was a contributor to the formation of petroleum.

It would thus appear to be of special interest to study the composition and chemistry of algal fatty components in order to discover the mechanism of their transformation into hydrocarbons.

The characteristic colours of oils might similarly be traced to the pigments which are so prominent a feature of these natural oils.

The theory of Murray Stewart [28] that the crude oils of Burma owe their origin to the natural oil secreted by dipterocarpus trees, appears to receive some amount of confirmation from the results of the present investigation, as does also the theory as set forth in his book [29] relating to the silicification of the wood, except that, as shown by the present writer, complete molecular replacement of the wood substance by silica need not necessarily have taken place, since the oil was able to capture and retain an intermediate stage.

Here also is indicated a subject for further research involving a chemical investigation of dipterocarpus oil in order to trace its conversion into petroleum.

The presence of resins in a large number of crude petroleums is another subject which invites further investigation.

As regards the application of the microscope for purposes of correlation, there is evidently a wide field for further research. Mention has already been made of the possibility of characterizing oils by means of the types of organism of which they carry the preserved remains. Some results have already been secured also by the comparison of well cores with the oils derived from the same formation. This type of correlation could be carried further and the microscopic examination of cores extended to the smaller fauna and flora, which in the routine method of examination frequently escape observation.

The theory of A. Wright and P. W. K. Sweet [30] that the jurassic is the source of oil both in Cuba and Mexico, as well as Colombia, Venezuela and S. Western Texas, may receive some confirmation from the results of the present study. According to this theory, the jurassic oil has been driven from its source beds into overlying strata as a result of igneous intrusion. Now, the coke-like fragments found by the author in a sample of jurassic oil in Mexico may well represent the product of such intrusions. Further, it was observed that in several cretaceous Mexican oils, the chitinous limbs of an insect similar to acarina were found, and in a core, taken from the jurassic producing formation of a well, the whole insect was discovered.

In the case of Roumanian oils there is a striking similarity between some of the organisms carried by oils producing from the miocene, and those carried by miocene oils in Mexico. This, however, is a matter for further research, since an insufficient number of Roumanian oils have as yet been examined to warrant any definite conclusions.

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# OBITUARY.

## WILLIAM HARDY MANFIELD.

By the death of William Hardy Manfield on August 13th at Portesham House, Dorset, the Institution has lost one of its oldest members. William Hardy Manfield was born in 1859, and was elected an Associate Member of the Institution in 1914, being transferred to Member in 1916. He was the great-great-nephew of Sir Thomas Masterman Hardy, Nelson's flag captain at Trafalgar. He was educated at Dulwich College and Pembroke College, Oxford, where he studied Chemistry with the late Professor Alfred Tribe. He early commenced a study of shales, on which he subsequently became an acknowledged authority. He carried out extensive investigations of the Kimmeridge shale deposits of Dorset, and was also called in to advise on the Scottish shale deposits. In 1911–12 he was Manager in France for the French shale Syndicate, opening up old mines and proving the extension of shale deposits. Returning to Dorset in 1913, he examined many processes for desulphurizing shale oils.

Throughout his life he maintained an active interest in the Dorset shale deposits and faith in the ultimate success of their development as an indigenous source of oil.

In 1916 Mr. William Hardy Manfield was placed by the Council of the Institution on the Panel of Oil Shale Experts recommended by them to the Government to report on Imperial Oil Shale Resources. Subsequent to the War, he devoted a considerable amount of time to local interests. At the time of his death he was Chairman of the Portesham Parish Council, President of the Village Institute, and President of Portesham Cricket Club. His reputation as a sportsman was widespread and in his early days he played Rugby for Somerset and cricket for Dorsetshire.

His loss will be deeply felt by many older members of the Institution, who will remember him as a staunch supporter of the Institution in its early days, and as a member of the Luncheon and Dinner Club which was active during the War and the years immediately following. Those who were privileged to visit his home at Portesham House will long remember the charming welcome of Mr. and Mrs. Hardy Manfield.

A. W. E.

# RESEARCH IN RELATION TO THE MOTOR VEHICLE.—FUELS AND LUBRICANTS.*

By F. H. Garner, Ph.D., F.I.C. (Member).

## Introduction.

Most of the knowledge of the requirements for motor fuels in spark-ignition engines, in so far as volatility is concerned, is based on the work of the Co-operative Fuel Research Committee,[1] itself a joint committee of the motor and fuel industries. In this particular work, various aspects from ease of starting to vapour lock were studied in turn. More recently, research has been concentrated more on lubricating oils than on fuels, and at present attention is being directed to the extreme-pressure lubricants necessary for hypoid and heavily-loaded bevel axle gears. In order, therefore, to present a broad summary of the progress in research as affecting fuels and lubricants, reference has been made to fuel research, much of which was carried out some years ago, but which is equally applicable to fuels of to-day. No attempt has been made to consider fundamental research on combustion, but the paper is confined to the results obtained by research on problems more directly connected with the practical operation of the engine.

Research on the combustion of fuels in internal-combustion engines has, during the last ten years, been more especially concentrated on studies of the engines themselves rather than of physical apparatus intended to simulate parts of the engine. As a result of the work during this period, a knowledge of the behaviour of fuels in internal-combustion engines has been developed, which can be correlated with laboratory tests with a reasonable degree of accuracy. Similarly, work on engine lubricating oils has led to the development of methods of testing, using engines under carefully controlled conditions, which in conjunction with a number of purely laboratory tests, have resulted in the markedly improved qualities of lubricating oils now available.

Close collaboration between engine manufacturers and fuel and lubricant producers has inspired this research work, which has contributed largely to the improved performance of the modern car as regards flexibility and freedom from trouble. The importance of such collaboration can be realized by the changes in the character of motor fuels over a period of years. It has been said that the car designer, in solving one problem, may create two new ones, and changes which have taken place in motor fuels have

* Paper presented at the Symposium on 'Research in Relation to the Motor Vehicle' at a joint meeting of The Institution of Automobile Engineers and other technical societies on March 2nd, 1937. The papers presented were "The Motor Vehicle," by C. G. Williams, "Fuels and Lubricants," by F. H. Garner and "Materials —with Special Reference to Steel," by T. Swinden, of which only the paper on "Fuels and Lubricants" is included here. The discussion which followed the Symposium has been abstracted so as to include only that relating to the paper on "Fuels and Lubricants."

introduced special problems from time to time. A demand from the engine designer for fuels modified to overcome certain limitations in engine performance has, of necessity, led to a variation in the character of the fuel in other respects, and thus in some cases an entirely new problem has arisen.

Supplies of fuel in the post-war period were of relatively poor volatility and, in consequence, engine manufacturers introduced the hot spot in

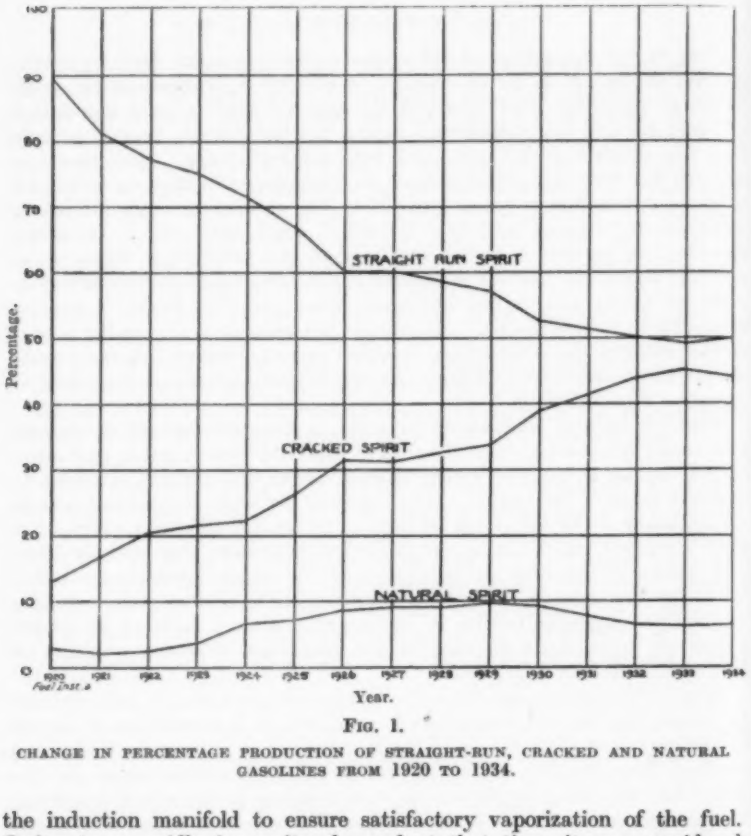


FIG. 1.

CHANGE IN PERCENTAGE PRODUCTION OF STRAIGHT-RUN, CRACKED AND NATURAL GASOLINES FROM 1920 TO 1934.

the induction manifold to ensure satisfactory vaporization of the fuel. Owing to a rapidly increasing demand at that time, it was considered that the tendency would be for fuels to become less volatile. The fuels were also of pronounced knock tendency and the work of Ricardo and Midgley showed that to obtain the higher efficiencies available with increased compression-ratios, improvements in anti-knock qualities were necessary. Petroleum fuels of high anti-knock tendency, and the use of lead tetra ethyl and benzole as additive agents were developed in the course of these investigations.

To meet the increased demand for motor fuel, cracking of petroleum products of higher boiling point developed rapidly, and it was later found that cracked fuels themselves were of good anti-knock qualities. Similarly, in order to improve the volatility, natural gasoline derived from natural gas was used, and the curve in Fig. 1 shows the approximate percentage of natural, cracked and straight-run petrol in motor spirit over a period of years from 1920 to 1934.

The motor fuels, both from cracking and from natural gas, were of higher volatility, and difficulty was experienced owing to vapour lock. This was caused by the formation of vapour from the fuel in the pipe leading to the carburettor, and more particularly in the carburettor, owing to the relatively high temperatures prevailing. Unsatisfactory performance at high speeds and bad idling were caused. At high speeds the vacuum at the main jet is increased, and at low speeds that at the auxiliary jet is increased, and this volatilizes the light constituents as bubbles, even in a fuel system designed mechanically to reduce the risks of vapour lock. It was therefore found necessary to eliminate a portion of the very light constituents of petrol, more particularly propane and butane, in order to prevent the formation of excessive quantities of vapour in the fuel system before the fuel reached the induction pipe.

Similarly, with cracked fuels, trouble was encountered owing to the formation of gum from these highly unsaturated spirits, and this led to alterations in chemical refining methods, and also to the addition of special chemicals known as inhibitors, which stabilize gasoline against gum formation even when it is stored for relatively long periods of time.

During recent years, with the more volatile fuels available, the fuel–air mixture is introduced into the engine at much lower temperatures and gives higher volumetric efficiencies, but further problems have arisen in connexion with octane number requirements. In 1932, road tests were made at Uniontown, Pa., to determine the most suitable method of operating the C.F.R. engine, so that octane numbers obtained in the laboratory test would correlate with the behaviour of the same fuels in cars on the road. A further series of road tests was made in 1934, and confirmed the earlier results. It has now been found that these conditions of test are no longer valid for cars operating under normal winter conditions, and that therefore some change is necessary in the method of determining octane number.

Thus, from time to time, special problems arise owing to changes in the engine or in the fuel required for the engine, and the importance of continuous collaboration between engine manufacturers and the manufacturers of fuels and lubricants is emphasized.

## Fuels for Petrol Engines.

One of the most important and difficult questions is the satisfactory supply of the fuel–air mixture to the individual cylinders of the engine; for ideal carburation each cylinder would receive correctly proportioned mixture at all loads and speeds, and this is far from being attained, as is shown by the carbon monoxide and oxygen contents of exhaust gas.

The characteristics dependent on volatility, which are of importance for motor fuels are, the following (see references 2 to 11) :—

1. Ease of starting;
2. Absence of vapour lock;
3. Rapid warming-up, satisfactory acceleration and idling and full development, at all speeds, of the corresponding maximum power;
4. Freedom from dilution of the lubricating oil;
5. Minimum fuel consumption.

As a result of modifications in the design of the fuel system—pumps, carburettors and induction manifolds—a very marked improvement has occurred in the last few years in the first four items mentioned, and to this the easy-starting fuels of controlled volatility now available have largely contributed. This, however, has not been accompanied by decrease in the fuel consumption, as will be seen from Table I, largely because, owing to the demand for flexibility, the fuel–air mixture supplied to the engine has been richer overall than that theoretically required for maximum economy.

TABLE I.

*Average Petrol Consumption for Various Horse-Power Classes from* 1931 *to* 1936, *Obtained from "The Motor" Road Tests.*

| H.P. | Miles per Gallon. | | | | | |
|---|---|---|---|---|---|---|
| | 1936. | 1935. | 1934. | 1933. | 1932. | 1931. |
| 8·0 | 38 | 43 | 42 | 41 | 41 | 45 |
| 10·0 | 30 | 30 | 31 | 30 | 30 | 30 |
| 12·0 | 27 | 26 | 26 | 28 | 25 | 27 |
| 14·0 | 23 | 23 | 24 | 24 | 25 | 24 |
| 18·0 | 20 | 19 | 19 | 20 | 18 | 18 |
| 20·0 | 18 | 18 | 19 | 18½ | 18 | 17 |
| 24·0 | 16 | 17 | 16 | 17 | 17 | 16 |

The carburation problem is mainly one of low speeds, or of rapidly changing speeds. The fuel–air mixture supplied to the engine under such conditions contains a proportion of unvaporized fuel, instead of a mixture of vaporized fuel and air, and the manifold has to guide the wet fuel in the proportion required for each cylinder. Observation of a vacuum gauge connected to the manifold shows the rapid variation of the pressure in the induction manifold during the operation of cars on the road, and if the inlet manifold is observed through a glass plate under varying throttle operations, surges of liquid are seen to be present in the fuel–air mixture, and this illustrates the difficulty under which the engine operates.

*Ease of Starting.*

It is somewhat difficult to separate the effect of the lubricant from that of the fuel in determining the ease of starting a car in cold weather, as admittedly the question of lubrication is the more important. The fuel–air mixture must be supplied to each cylinder to give an explosive mixture in the neighbourhood of the sparking plug. In starting, the engine is turning over at a low speed with a relatively high vacuum in the induction system, and a proportion of vaporized and atomized fuel

passes into the combustion chamber. The distribution may be relatively uneven between the different cylinders, and if the fuel is not sufficiently volatile, too lean a mixture may be present, and if too volatile, the mixture may be too rich, as the limits for an explosive mixture are relatively narrow, viz., 8 : 1 to 20 : 1.

There are certain differences in design between British and American carburettors, in that in this country auxiliary carburettors are provided for starting purposes, whereas in the States more importance is placed on the choke, which, in many cases, is fully automatic. The determination of ease of starting is a matter of considerable difficulty because of the variations in design of the fuel induction system, but as far as petroleum fuels are concerned, it is found that ease of starting correlated very well with the 10 per cent. evaporated point, or the percentage distilling off at 70° C. in the laboratory distillation range method, and is, of course, dependent on the atmospheric temperature. It has therefore been found necessary to modify the distillation range of motor fuels marketed in different seasons of the year, and accordingly in this country different volatilities are supplied for summer and winter, in order to ensure ease of starting in the winter, and freedom from the difficulties attendant on the use of too volatile a fuel in the summer.

*Warming-up and Acceleration.*

For satisfactory warming-up it is important that as soon as the engine has started the fuel shall be supplied in a condition so that it can readily be burnt and make the engine develop its full power. Any liquid fuel present in the air stream should be atomized as finely as possible, and as much vaporized fuel as possible should be present. Automatic heat control has been provided on some cars to accelerate the warming-up process, as at relatively low temperatures it is naturally desirable to use as little choke as possible in order to avoid the possibility of dilution of the lubricating oil.

If the fuel is completely atomized it burns equally satisfactorily as a mixture of vapour and air, but there is always the danger of the fuel settling out, especially at points where the fuel stream impinges directly on any solid surface, with the consequence that too lean a mixture is supplied to the combustion chamber, and liquid may reach the cylinder and wash the walls free from lubricant. The warming-up period can be considerably reduced by providing excess heat, but the introduction of such excess heat may cause a considerable loss in power and also an increased tendency towards pinking. The provision of by-pass valves in the cooling water system is also of importance in reducing the warming-up period.

Similarly, after the engine is thoroughly warmed-up it must respond rapidly to the throttle and give smooth acceleration without any flat spots. When the throttle is suddenly opened the suction is reduced, and it is now usual for extra fuel to be supplied at commencement of acceleration. Here, again, the hot spot in the inlet manifold serves to vaporize the liquid fuel interjected from the auxiliary supply into the air stream when the throttle is rapidly operated.

The experimental work of the Co-operative Fuel Research Committee showed that maximum acceleration can be obtained with any fuel, but if the fuel is of low volatility, a richer mixture is required. However, the design of the induction system appears to be the deciding factor rather than the fuel, but it is perhaps easier to secure good acceleration with a more volatile fuel, since it is easier to control the mixture ratio. The 50 per cent. point in the distillation range of the motor fuel appears to be an index of ease of acceleration and warming-up characteristics, subject to the above consideration.

*Vapour Lock.*

Vapour lock shows itself by an interruption of the normal liquid flow of the fuel, and is due to vaporization of the fuel, either before or in the carburettor. There are two forms, one in idling or in light traffic, shown by "stalling" followed by difficulty in starting, and the other at higher speeds, loss of power similar to that felt in momentarily running out of fuel. Vapour may be formed because the fuel pipe between the tank and the pump is heated, but this has in large measure been overcome by the design of pumps capable of handling many times the maximum fuel requirements of the engine. Vapour may also be formed in the fuel line from the pump to the carburettor (usually by heat from the exhaust manifold), and this may lead to uneven flow, since 1 volume of petrol may give as much as 200 volumes of vapour. The importance of providing a satisfactory vent in the carburettor for the vapour has been realized, but the loss of fuel in this way may on occasions be quite substantial, up to 10 to 20 per cent. Starting difficulties also may be increased, since the fuel remaining in the carburettor may have been deprived of the light fractions essential for easy starting. Further, if vapour lock is present, it is difficult to maintain a satisfactory fuel–air ratio, as the mixture may be too lean if the petrol vaporizes in the jet or too little is pumped, and may be too rich if liquid is forced into the carburettor jet owing to pressure caused by vaporized fuel in the carburettor float chamber.

Vapour lock is not usually of great importance in this country, largely owing to the grades of fuel marketed, but both for this country, and especially for the export market, where a much wider range of temperature will be encountered than in the British Isles, it is undoubtedly important to ensure that all parts of the fuel system are kept at as low a temperature as possible, in order to minimize any vaporization of the fuel before leaving the carburettor jet. Vapour lock is more serious in commercial cars, since the under-bonnet space may be fairly completely filled with engine and accessories and the temperature may be very high.

The tendency has been towards more volatile fuels, and these are necessary to give satisfactory idling and general operations with the newer types of fuel system. The limiting factor, from the point of view of the refiner, both as regards quality and economy of fuel, is the necessity of limiting the volatility of the fuel as indicated by vapour pressure and percentage distilling over at low temperatures, since these factors determine the rate of vapour formation at the temperatures existing in the fuel system.

*Dilution.*

At the present time, with the more appropriately volatile types of fuel available, dilution cannot be considered of serious importance, and in general a figure up to about 5 per cent. is reached within the first 400 or 500 miles under normal temperature conditions in Great Britain and maintained at about this figure during the continual operation of the car. The amount of dilution is dependent on atmospheric temperature, and, more particularly, on the temperature of the crankcase oil under driving conditions. Difficulty is, of course, still encountered when kerosine or products of even higher boiling points are used in engines not specially adapted for such fuels. The adoption of crankcase ventilation has helped considerably in the elimination of dilution, and has also helped to maintain the lubricating oil free from deleterious products formed in the crankcase. The 90 per cent. point in the distillation range is the limiting factor in determining dilution.

*Anti-Knock Qualities and Road Ratings.*

Reference has already been made to the work of Ricardo, and Midgley and Boyd, in demonstrating the importance, from the point of view of efficiency, of the anti-knock qualities of petrol. The introduction of lead tetraethyl has been of the greatest importance in this connexion, but the refiner has also developed methods of cracking to give fuels of high octane number, including the later development of reforming, which consists in cracking of heavy ends of petrol to more volatile products of good anti-knock quality. In this connexion, the more volatile constituents of petrol are also supplied from natural gas, and these, in themselves, are of good anti-knock quality. A more recent development is the introduction of polymerization, in which gases obtained from cracking operations are transformed into liquid products of high octane number.

The adoption of the Motor Method, using the C.F.R. engines, under carefully defined conditions, to determine octane numbers, was the result of a very complete programme of experimental work at Uniontown in 1932, confirmed by a further correlation with cars on the road in 1934. It appears, however, that in more recently built cars the relative anti-knock ratings of fuels are sensitive to changes in atmospheric temperature, and in a recent note the Ethyl Gasoline Corporation points out certain recent trends in engine design as contributing factors: improved cooling, such as full-length water-jackets and directed water circulation, and also reduced heating of the inlet manifold and lower carburettor air temperature in cold weather due to the increased adoption of by-pass water circulation instead of radiator shutters.

At the recent S.A.E. Meeting in January, Campbell, Lovell and Boyd [12] showed that fuel "depreciation," *i.e.*, behaviour in the engine as though the fuel is of lower octane number than that obtained by the Motor Method, may be affected by engine speed and mixture ratio, and they quote an instance where an apparent depreciation of 5·5 octane numbers was brought about merely by enriching the mixture ratio from 14 : 1 to 11 : 1. Table II shows the effect on the apparent knock rating of two fuels under different conditions of test:

TABLE II.

| Fuel. | Method. | | | |
|---|---|---|---|---|
| | C.F.R. Research. | A.S.T.M. | Road, Standard Spark. | Road, Modified Spark. |
| 100 per cent. cracked gasoline . | 79·9 | 70·7 | 66 | 80 (approx.) |
| Commercial blend . . . | 71·5 | 69·3 | 68 | Not rated |

Appreciation or depreciation is partly due to the reference fuels on which the octane numbers are based, although equally important is the fact that the apparent rating may be affected by the chemical composition of the fuel.

*Economy.*

Closely connected with the necessity for supplying a rich mixture to enable maximum performance to be obtained is the question of economy of fuel. Mileage per gallon varies widely according to the road conditions, and Platt [13] quoted figures for a 20-h.p. saloon car which varied from 9½ m.p.g. during a long ascent of 1 in 15 to 1 in 10, to 13 m.p.g. in heavy city traffic, up to as high as 22½ m.p.g. for a level road speed of 25 m.p.h. The whole fuel system between tank and engine is important in fuel economy, as poor mileage may be partly due to vapour lock, but is due more particularly to the necessity of supplying rich mixtures to ensure that combustible mixture is supplied to each cylinder at all speeds, and to give rapid acceleration and flexibility in traffic. Maximum power is developed at about 12 : 1 by weight, whereas for greatest economy the air–fuel ratio is about 15 : 1 by weight.

In general, fuels of low volatility derived from petroleum have a higher specific gravity and lower calorific value. However, the difference in B.Th.U. available between such fuels is too small to be of importance in economy of fuel, as with more volatile fuels greater economy and power can be obtained, since lower manifold temperatures prevail with consequently a greater charge of fuel being fed into the engine.

Taub, in a recent paper before the Society of Automotive Engineers,[14] stated that present fuel consumption in U.S.A. was no better than it was five years ago, and attributed this largely to the higher road speeds of the present day. He pointed out that by proper adjustments of the tappets, sparking plug gaps, and spark advances, 10–15 per cent. improvement in fuel economy may often be obtained. J. B. Macauley [15] pointed out that by sacrificing acceleration and limiting maximum road speed, as much as 30 per cent. in economy may be gained; he quoted figures on part throttle over a speed range of 20–60 m.p.h. of 18·4 m.p.g. as against 8·4 m.p.g. on wide open throttle over the same speed range. The introduction of overdrives for passenger cars and of governor carburettors for commercial vehicles offers the possibility of economizing fuel consumption by reducing operation at high engine speeds.

At this point a brief reference may be made to the equipment designed for the investigation of fuel and lubricant performance in the motor car

engine. The road test room at the Esso European Laboratories is illustrated in Figs. 2, 3, and Plate I. Starting tests on petrol can be made at temperatures as low as — 10° F., and the room can also be warmed up to 120° F.

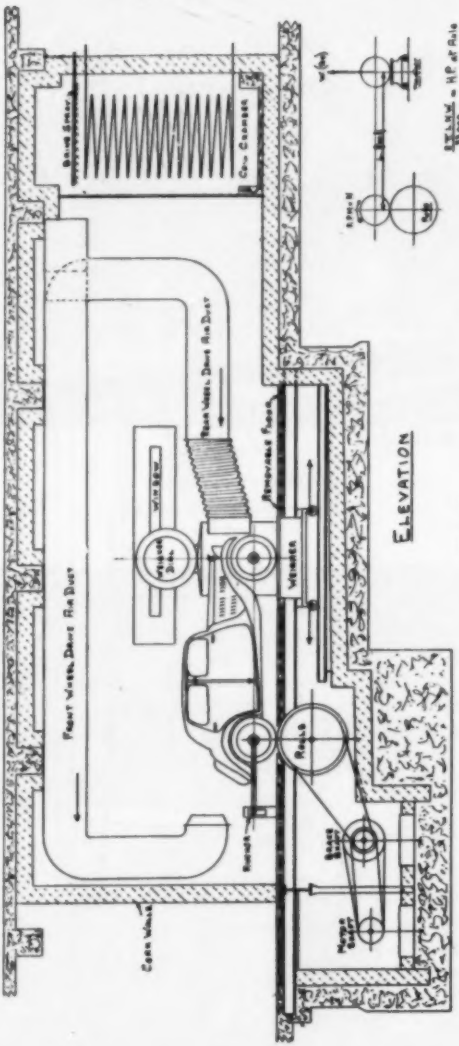


FIG. 2.
DIAGRAMMATIC LAYOUT OF ROAD-TEST ROOM ELEVATION.

for duplication of high temperature conditions. Other equipment in this connection is shown in Fig. 7, Plate II.

The equipment consists of a chassis dynamometer in an insulated chamber

with arrangements for absorbing power from the driven axle of the vehicle on test or supplying power to the driving-wheels for motoring tests, a refrigerating plant for the control of the room temperature, and fuel and

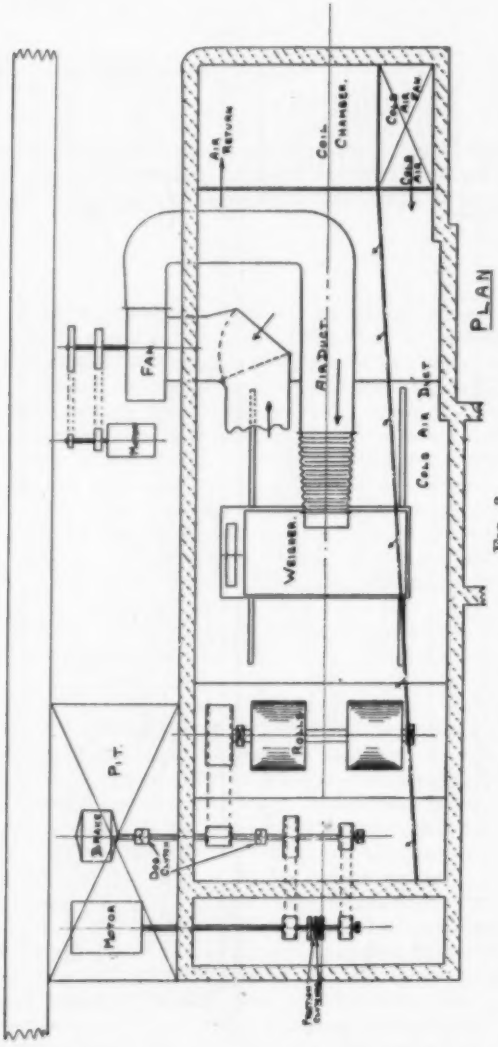


FIG. 3.
DIAGRAMMATIC LAYOUT OF ROAD-TEST ROOM PLAN.

exhaust services. The chassis dynamometer comprises a pair of rolls on which the driving-wheels of the vehicle rest, the rolls shaft being belt coupled to either a water brake for power absorption or, alternatively,

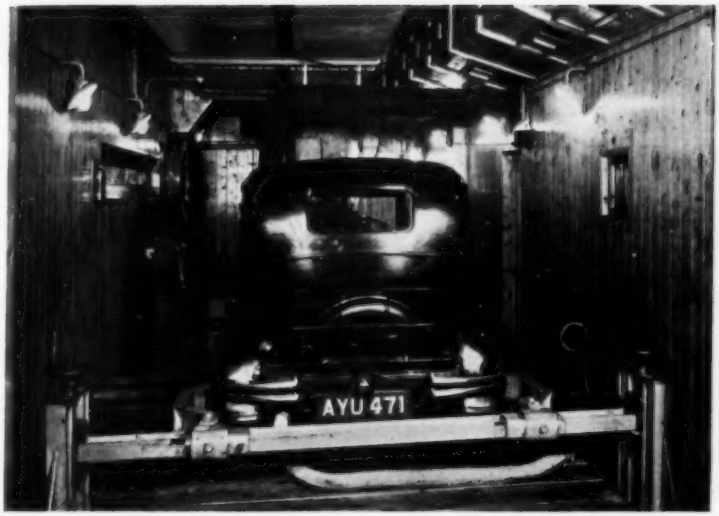


FIG. 4.
ROAD-TEST ROOM.

FIG. 5.
ROAD-TEST ROOM.

[*To face p.* 584.

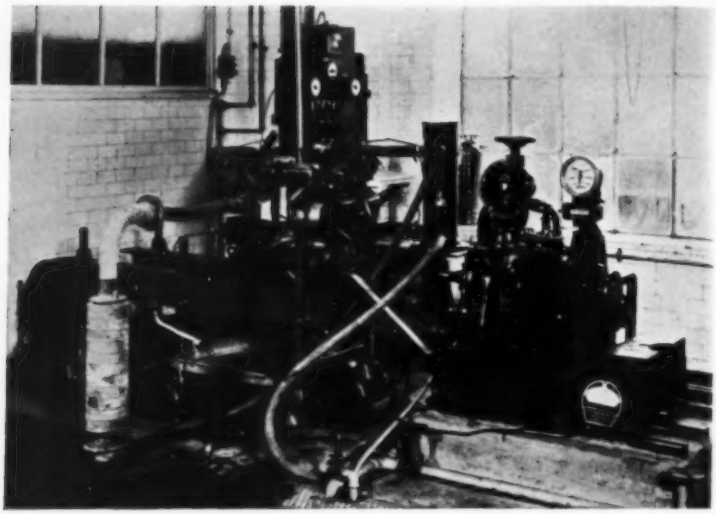

FIG. 6.
ENGINE AND BRAKE FOR LUBRICATING OIL TESTS.

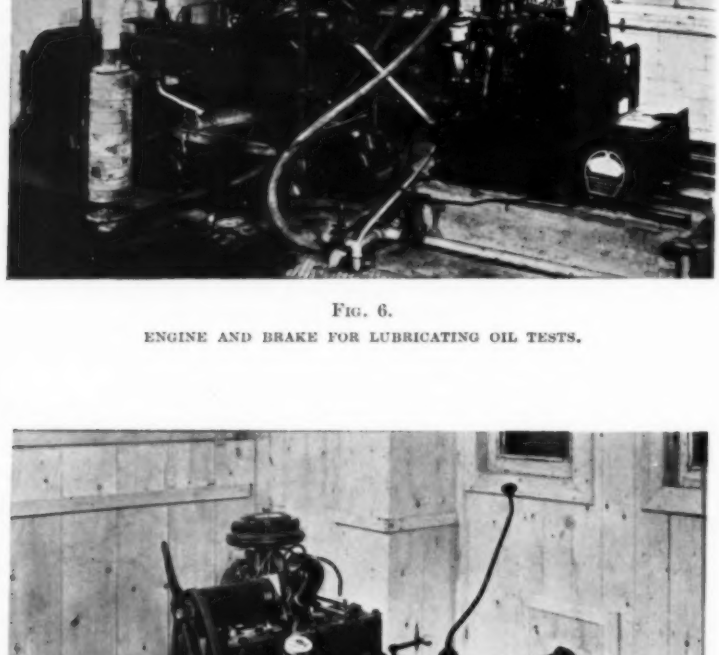

FIG. 7.
ENGINE IN COLD ROOM FOR STARTING TESTS.

to a variable-speed motor through countershafts for motoring tests. Air is delivered from a nozzle to the radiator of the car at any speed up to approximately 70 m.p.h. When the room is being operated at low temperatures the air of the room is circulated over the evaporator coils of the refrigerator, as shown in Figs. 2 and 3.

Fig. 2 is a diagrammatic layout of the road-test room and the illustration shows a car with the rear wheels on the rolls and the front wheels on the weighbridge. The H.P. may be calculated from the wheelbase, the r.p.m. of the rear wheels, and the relieved load measured on the weighbridge.

No reference has yet been made in this paper to fuels containing alcohol which have been investigated largely from the point of view of propaganda for or against. From the technical point of view, much depends on the basis of comparison, and a summary of experimental work on engine and road tests will be found in a recent article by O. C. Bridgeman, of the United States Bureau of Standards, in which ease of starting, warming, acceleration, vapour lock, engine power, and fuel consumption are all discussed.[16]

## Fuels for Compression-Ignition Engines.

For heavy commercial transport the compression-ignition engine is rapidly assuming the predominant position as compared with the petrol engine in this country, and in France and Germany long-distance commercial transport and omnibuses are almost entirely operated by compression-ignition engined vehicles. The development of high-speed compression-ignition engines in road transport in U.S.A. has been less rapid than elsewhere, and it is only during the last year or so that there has been any marked increase in the number of such vehicles.

The most important characteristic of diesel fuels is probably that of Ignition Quality, and research carried out in Great Britain has been responsible for much of our knowledge of this property. A number of purely laboratory tests have been devised in order to measure ignition quality, but although some of these, in particular Diesel Index and Aniline Point, serve as useful general guides on normal fuels, they may on occasions give results which are widely different from those in the engine. In a similar manner to the octane numbers adopted for expressing the anti-knock qualities of petrol-engine fuels, cetene numbers were proposed for rating the ignition quality of diesel fuels, the cetene number being based on blends of cetene, which is an unsaturated hydrocarbon obtained by the distillation of spermacetti, and alpha-methylnaphthalene, a synthetic chemical derived from naphthalene.

More recently, the use of cetane, a saturated hydrocarbon, has been considered in place of cetene, and it has been adopted as a primary reference fuel for the last two years by the American Society for Testing Materials.

Methods for the determination of the ignition quality of diesel fuels have not been fully standardized, but investigations in this country and in the United States have resulted in two tentative methods being put forward.

At a meeting of the Institution of Petroleum Technologists in Holland in May 1936, which was devoted to diesel fuels, it was shown that tests made under running conditions gave good agreement, even when many

engine types were used, and that more concordant readings were obtained with the three-engine types—Gardner, A.E.C., and Ricardo—than with the modified C.F.R. oil engine. Starting tests on the Gardner engine gave ratings for ignition quality on petroleum diesel fuels which agreed well with tests made under running conditions, but only when the tests were made by reference to secondary standards; the primary standards used, cetene and alpha-methylnaphthalene, were affected more by both changes in engine and change of operating conditions than were the secondary reference fuels.

A tentative method for determining ignition quality, recently put forward by the Institution of Petroleum Technologists, allows any type of oil engine to be used, and states that ignition quality is not affected to any appreciable extent by the engine conditions used, provided the tests are on petroleum fuels and that "doped" fuels are not included. Two methods are permitted: (1) a running test based on delay angle measurement, and (2) a throttling test depending on the variation in the inlet depression caused by throttling down the engine until misfiring occurs. The second method is less accurate than the first, but no elaborate instruments are necessary, and for both methods secondary reference fuels are recommended rather than the primary standards—cetane or cetene and alpha-methylnaphthalene.[17]

The American Committee, in their tentative method, adopted cetane and alpha-methylnaphthalene as the primary standards, but used secondary reference fuels for tests. This method of determining ignition quality is based on the delay angle, using the modified C.F.R. engine fitted with bouncing-pin.[18]

For both methods an accuracy to $\pm$ 1·5 cetane numbers is obtainable, but in the first I.P.T. tentative method an accuracy of $\pm$ 0·5 is claimed with a particular engine under specified engine conditions.

The question of fuel economy is one of great importance with oil engines, although no gain in efficiency may be obtained by the supply of fuels of better than the necessary quality; that is, of higher cetane number than required by the engine. However, the use of these higher-quality fuels, if generally available, would enable lower compression-ratios (and possibly higher speeds) to be used in the oil engines and, therefore, some saving in weight.

A recent survey of oil-engine design on the Continent and in Great Britain indicated different trends in the various countries, and this appears to be related to the question of fuel quality. In this country the present tendency appears to be towards the wider use of the direct-injection type rather than the ante-chamber design for road transport, largely owing to the greater economy of fuel experienced with the former type. The direct-injection engine is, in general, more sensitive to the quality of the fuel available than the ante-chamber type, and it would therefore seem that the reason for this trend is the importance of fuel economy in this country owing to the high Government tax of 8*d*. per gal. on the fuel, but this trend would not be possible except with the high-quality fuel. At the present time, the diesel fuel supplied in this country is of excellent ignition quality, and when engines of British make are exported to the Continent or to the Dominions, difficulties may occasionally be met owing to the use of fuels of inferior quality.

In Germany, on the other hand, the tendency appears to be in the direction of ante-chamber types, and such engines can use lower-grade fuels than are desirable for direct-injection engines, but this is countered by the generally poorer fuel economy obtained with this type of engine.

Fuel quality is a factor of great importance for the export market of oil engines and also in connexion with supplies. The continued increase in oil engines on the road may present difficulties also as to future supplies, as the types of diesel fuel available in large quantities are of relatively poor ignition quality. The application of hydrogenation is one method of producing diesel fuels of good ignition quality; but, inasmuch as light diesel fuel at the present time is not chemically refined, special processes necessary for improving ignition quality must inevitably add to the cost.

Boerlage and Broeze, from their experimental work, showed that the maximum power output is sometimes lower for fuel of high than for fuel of medium ignition quality, taking as criterion the visibility of the exhaust. With a very short ignition delay period combustion of incompletely mixed fuel and air may take place; the higher power output is obtained at the expense of slightly rough running which would be disadvantageous for road vehicles.

A further point on which research has been carried out in recent years is the inter-connexion between viscosity and efficient supply of the fuel to the engine; it is found that for normal petroleum diesel fuels it is unnecessary to fix a lower limit, since with such fuels the type of pumps used on oil engines is efficiently lubricated. The viscosity, however, must not be so high that there is difficulty in supplying the fuel to the engine, and the recent specification issued by the British Standards Institution specifies a maximum of 45 sec. Redwood at 100° F.

There appears to be no general agreement on the significance of distillation range as a factor affecting the behaviour of diesel fuels in the engine. Fractions from a given crude of different distillation range may show wide variations in ignition quality; it is important to eliminate high-boiling constituents from the oil, and for this purpose the new British Standards specification suggests the figure of 85 per cent. minimum distilled at 350° C.

## Lubricants.

### *Engine Lubricating Oils.*

Systematic investigation of lubricating oils under operating conditions has been the subject of many studies in recent years, and our knowledge of their behaviour is dependent on engine tests, as distinct from physical or chemical tests, to a much greater extent than with engine fuels. Much labour and ingenuity have been devoted to the development of laboratory oxidation tests intended to duplicate the deterioration of the lubricating oil under engine conditions, and from time to time one or other of the many tests has met with partial acceptance. It appears that none of these tests can be considered as giving a complete knowledge of the deterioration of oils in engines, although at least two of these, the Air Ministry Oxidation Test and the Sligh Test, give information which may serve as a valuable guide.

In considering the behaviour of lubricating oils in the motor-car engine, the following are of most importance :—

1. Ease of starting in cold weather;
2. Satisfactory lubrication of the engine, which includes relative freedom from deterioration in use; freedom from sludge formation and the formation of carbon in the engine; and no harmful action on the bearings or any other part of the engine, and, in short, absence of wear;
3. Minimum oil consumption, consistent with adequate lubrication.

The important question of cylinder wear has been discussed in the previous paper by Mr. Williams.

One of the questions on which research has been concentrated in recent years has been the ease of starting in winter weather, and this work has given information on other subjects, more particularly on suitable viscosities for the lubrication of engines, and on engine wear. It is only by the recent development of newer methods of refining that oils have become available with the relatively low change in viscosity with change in temperature necessary for easy starting. The term " Viscosity Index " [19] has been widely adopted as a method of expressing the viscosity–temperature relationship of lubricating oils, oils of high viscosity index having a relatively low change in viscosity with temperature, and oils of low viscosity index having a relatively high change with temperature.

Blackwood and Rickles [20] investigated a number of American cars at different temperatures using oils of various viscosities, and found a cranking speed of at least 35 r.p.m. to be desirable in any car under the most unfavourable conditions of temperature anticipated. Cranking speed is the controlling factor in cold starting, since the speed may be too low for distribution of combustible mixture to all cylinders.

There was found to be an extremely wide variation from car to car, depending on the relationship between starting motor torque and the torque necessary to turn the engine at the required speed for starting, and it should be noted that even above 0° F. with oils of high viscosity the frictional resistance of the crankcase lubricant may be greater than the full torque that the engine can develop.

Other factors of importance are the fuel and the efficiency of the fuel system, to which reference has already been made, and also the efficiency of the ignition system, as at low temperatures the battery output is considerably reduced.

Barrington and Lutwyche,[22] as a result of their investigations, stressed the importance of low-viscosity oil for starting and also pointed out that low-viscosity oils were not disadvantageous when hot. They drew attention to the relatively high cranking speed required by British cars, and quote a figure of 60 r.p.m., as against the figure of 35 r.p.m. which is suggested by Blackwood and Rickles (based on their experimental work with American cars) as being desirable. They found that breakaway torque was usually twice that necessary to maintain motion. Both papers directed attention to the importance of minimizing any possible resistance between the battery and the starting motor, either by reduction of the cable length, or by paying special attention to terminal design.

For easy starting, the use of oils of sufficiently low viscosity at the prevailing temperatures is most important, and the viscosity of the lubricating oil is intimately related to the consumption of oil in engines. There has been a tendency towards the use of low-viscosity oils for the lubrication of motor-car engines, more particularly in America, and there is no doubt that the time is overdue for a similar change in this country.

Viscosity in this country is usually expressed in time in seconds flow with the Redwood instrument at 140° F., and while oils of much lower viscosity at this temperature than are being used at the present time in this country are desirable from the point of view of reduction of engine friction and wear, special importance attaches to a high viscosity index—that is, relatively little change in viscosity with temperature, as will be realized by comparing this temperature of 140° F., on the one hand, with a temperature of 25° F., which can be taken as representing cold conditions in this country, and, on the other hand, with a temperature of 350° F., which can be taken as the piston skirt temperature, which is of great importance in considering the question of oil consumption.

For ease of starting, the lower the viscosity of the oil at 25° F., the less is the power required from the battery when starting, and the greater the assurance that the oil will be supplied in satisfactory quantities to the bearings and cylinder walls in order to ensure a film of lubricating oil being present on the wearing surfaces. The flow of oil to the bearings may be prevented at low temperature by the presence of paraffin wax in the lubricating oil, and by the use of Paraflow [23] it is possible to reduce the pour point of paraffin base oils and obtain the advantage of low pour-point oils, without impairing other desirable characteristics of such oils. Blackwood [21] indicates that for a minimum cranking speed of 40 r.p.m., the maximum viscosity which can be tolerated in the lubricating oil is 23,000 Saybolt seconds at 0° F. (20,000 Redwood seconds or, 5,000 centistokes), but this varies from 13,000 to 44,000 Redwood seconds with temperature range from − 20° F. to + 50° F.

For low oil consumption, the high temperature mentioned—namely, 350° F.—is important; again, high-viscosity index oils are advantageous, since such oils maintain their viscosity at these high temperatures and thereby consumption may be markedly lowered and, further, blow-by of the burning charge is also reduced, with correspondingly less deterioration of the oil. The improvements in the viscosity index of the oils have been achieved, first, by changes in the method of refining, of which one of the first processes adopted was hydrogenation, and, more recently, by the various solvent refining processes. Still more recently, Paratone [24] has been developed, the addition of which in small proportions to lubricating oil causes a marked improvement in the viscosity index.

Since oils of high-viscosity index have correspondingly high viscosities at high temperatures, the grade of oil used can be of lower viscosity at ordinary temperatures (as specified, for example, in Redwood No. 1 sec. at 140° F.).

The ability of lubricating oils to stand up under severe engine conditions is, as already pointed out, effected partly by the viscosity characteristics, but much depends on the type of crude and method of refining.

Carbon residue, as determined by the Conradson or Ramsbottom tests,

has been compared with the amount of carbon formed in the engine, but other factors are of importance, notably the mechanical condition and design of the engine and the viscosity of the oil. As a measure of deterioration of lubricating oils in use, much attention has been, and is being, devoted to the development of suitable oxidation tests, but at the present time the only completely satisfactory tests are engine tests, and these, in general, consist of fairly long runs during which some particular aspect of the engine condition is emphasized according to the problem which is being investigated.

Fig. 6, Plate II, shows an engine on the bench connected with a Heenan and Froude water-brake, designed for tests on motor lubricating oils. The engine illustrated operates for a period of 3 min. idling, followed by 17 min. full load, and this cycle is continued for 50 hrs. Provision is made for the engine to the automatically shut down if the speed rises over 3000 r.p.m., of if the water or oil temperatures rise above a predetermined figure. In case of fire, arrangements are made for the petrol supply to be cut off, and the whole apparatus is protected by a fusible link which releases carbon dioxide gas through funnels, not only on to the engine, but also into the exhaust trench.

*Sludge Formation.*

At the present time any foreign material in a used lubricating oil is likely to be described as sludge, although it may vary from the thick emulsion sludge largely composed of emulsified oil, water, and carbon, to a thin, hard lacquer. For this reason, the discussion at a recent meeting of the Institution of Petroleum Technologists of nomenclature for sludges and deposits in engines is of special interest, since an accurate description is always of assistance in the ultimate solution of the problem. It is generally agreed that sludge deposits are dependent on the formation of oxidation products composed of asphaltenes or acidic materials. These act, together with " carbon," as emulsifying agents for the oil, water, road grit, and metal particles. The water present may be derived from the cooling system, but low atmospheric or cooling water temperatures are conducive to crankcase condensation of water from the atmosphere. In many cases, owing to the mechanical condition of the engine, water derived from the combustion products may be the source of part of the water in emulsion sludges. The Indiana oxidation test, which employs a similar apparatus to the Air Ministry test, except that a lower temperature (341° F., as against 392° F. (200° C.)) is used, and that asphaltene determinations are made on the oxidized oil instead of viscosity and Ramsbottom carbon, was put forward as a method of determining the tendency of motor oils to form sludge in use.[27]

Blow-by of the hot combustion gases past the piston may cause marked deterioration of the crankcase oil and increase ring sticking and sludge formation.

*Bearing Corrosion.*

During last year it appeared that bearing corrosion might become a serious problem in the United States, since, owing to the high crank-

case oil temperatures found on certain cars, some of the more highly refined lubricating oils became oxidized with the formation of acids and oxidation products which corroded some of the newer types of bearing metals, such as those containing cadmium or of high lead content. However, considerable progress has been made on this particular problem by decreasing crankcase temperatures, and a further study of the new types of bearing metals and lubricating oils being used.[28]

*"Oiliness Agents."*

No reference has so far been made to "oiliness agents," but a difference, of opinion exists as regards the necessity of such addition agents in the ordinary lubrication of engines, and a sub-committee of the Society of Automotive Engineers is investigating whether overall improved performance does result.

For new engines, however, it has been found that such additions do help in the running-in process. In the last Wilbur Wright Lecture, Pye, in pointing out that perfect lubrication is vital to the engine, stated that in so far as aero engines are concerned the maintenance of slippery surfaces under the arduous conditions of the modern engine was likely to influence design and even to become the chief factor in engine development.

*Oil Consumption.*

The importance of high viscosity index in connexion with oil consumption has already been discussed, and in so far as the oil is concerned, viscosity at engine temperature is by far the most important. The main causes for high oil consumption, apart from the mechanical condition of the engine, are high engine speeds and oil leaks, and the viscosity of the oil plays an important part in both of these, since at greater engine speeds the temperatures are higher and the importance of suitably high viscosity at high temperatures is again stressed.[25] Furthermore, the oil throughput is increased, more particularly by the oil pump, and the greater oil flow through the bearings also tends to increase consumption; at higher speeds, more oil is present in the form of spray, with the result that the lubricating oil losses are greater. However, economy achieved in low oil consumption, if this is effected by the use of oil of high viscosity at working temperatures, may be outweighed by the cost of the greater amount of fuel necessary to overcome increased engine friction and the possibility of greater engine wear.

In this connexion Frolich [26] pointed out that in comparing two oils of identical viscosity at 0° F., but with viscosity indices of 50 and 120 respectively, the consumption at 50 m.p.h. with a 50 V.I. oil was approximately 0·6 Imperial gallons per 1000 miles, as compared with 0·35 Imperial gallon per 1000 miles for the 120 V.I. oil.

## Extreme Pressure Lubricants.

One of the more recent developments is the increasing attention paid to the use of hypoid gears for rear axles owing to the possibility of lowering the propeller shaft and thus permitting a low, flat floor to the car, but in addition, advantages are claimed for quieter transmission.

Wolff [29] states that the maximum stress on the gear tooth surface may reach values of 350,000 to 400,000 lb. per sq. in. and rubbing velocities up to 1800 ft. per min., with the result that scoring and scuffing of the tooth profile surfaces are caused by actual welding of small areas along the tooth contact line under the high local surface temperature conditions. Two types of lubricant have been developed, of which the earlier type was the so-called "mild hypoid lubricant," but which was not a true extreme-pressure lubricant suitable for hypoid gears which demand a powerful extreme-pressure lubricant to carry the loads. The setting up of standards of measurement has proved very difficult, but as a result of an extended research programme, a machine has been developed by the S.A.E. Standards Committee, and it is now hoped that this machine will soon be available for classification of such lubricants into two types, one suitable for spiral bevel gears which do not need the more powerful type of lubricant, and the other suitable for hypoid gears.[30] It is pointed out that the latter type of lubricant, although it blackens copper, does not corrode axle parts in service, either in the presence or absence of water.

## Conclusion.

Developments have also occurred in the lubrication of other essential parts of the modern road vehicle, principally in the direction of providing lubricants of lower viscosity suitable for modern transmission of greater complexity and lower weight, and also in the direction of simpler lubrication.

It has been possible to discuss only certain phases of the subject in this paper, and only brief reference has been made to the development of methods of investigation, which is one of the most important items of progress in research, and no reference has been possible to fundamental research either on combustion or on lubrication.

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## *DISCUSSION.*

Sir William J. Larke (Chairman): With regard to lubrication, which has been dealt with by Dr. Garner, as a car user I think that all car makers, and the oil companies as well, should collaborate by insisting that car users should change their lubricating oils winter and summer. No doubt a great many of our starting troubles are due to the fact that the average car user pays no attention to his car at all and uses the same type of oil in winter as in summer. I support entirely the remarks on the necessity for studying the question of starting. Nothing is more exasperating to the ordinary car user than difficulty in starting a car for which he has paid a high price.

Mr. T. Thornycroft: With regard to Dr. Garner's paper, it is all very well to say we should have fuels to suit different climates, the summer and the winter; but we have to allow for the user. As Sir William Larke has said, it is really essential to use different oils in winter and in summer,

but when I have complained to some quite reputable people who have been operating heavy motor vehicles that they were using a much too heavy oil in the winter, they have replied that they have not yet used up their summer oil, so that they could not use the winter brand! That is not an isolated case, but a very ordinary one. I am not sure that it was not one of our very large transport concerns; it might even be connected with some of the people who run vehicles on rails. (Laughter.) I personally believe that we should produce an engine which will run always on a reasonably light oil, and employ an oil which we can use both in summer and in winter. I have been a great pusher of the light oils, and I am glad to notice that the use of the light oil is proving correct.

With regard to the petrol problem, I think we have to produce a vehicle that will start on almost any fuel. I remember that in the early days of the automobile we had what we used to call the 6/80 spirit, which was very light and volatile. As spirits became worse we found that we could not use the old carburettors that were used previously. To-day we have to improve the engine and the carburettor and the whole system, so that starting can be achieved on almost every fuel. I personally have found remarkably little difference between summer and winter grades supplied at various filling stations; actually I think there is a certain amount of mythology about some of these things. (Laughter.)

Finally, I should like to emphasize again the great benefits that the Industry can gain from co-operative research.

*Mr. Alex. Taub spoke at this stage. His comments are embodied in his written contributions subsequently received.*

Mr. J. Kewley: The subject of fundamental research has rather been slurred over to-night. It was mentioned casually by Dr. Garner, but otherwise it has been sadly neglected; therefore, I should like to make a plea for it. Fundamental research gives us new tools, which, as soon as they have been developed, lead to extraordinary further developments. Such a new tool is that which I had the pleasure of seeing in operation in the Laboratory of General Motors last September. One of the most fascinating experiences I have ever had was to see the explosion wave in a motor cylinder just under my nose through a complete quartz cylinder top; a slow-motion picture was also thrown on to a screen so that the actual progress of the wave could be seen under detonation and non-detonation conditions. It was possible to see the point at which the detonation wave started and came back to meet the advancing normal combustion wave. Work on similar lines is being done in Holland. The new cathode-ray oscillograph has very much simplified the problem of obtaining indicator diagrams, and there is every reason to believe that before long the piezo-electric effect of the quartz crystal will be so well developed that we shall have the perfect indicator, without any inertia lag at all. Such a tool will give us a clearer insight as to what is taking place in the cylinder.

One other new tool I should like to mention—leaving out of consideration the use of X-rays for crystal analysis, which is throwing much light on the constitution of alloys—is the electron diffraction method. Pro-

fessor Finch of the Imperial College, South Kensington, who has done some interesting work, permits me to tell you something about it. A beam of electrons really behaves as a radiation of extraordinarily short wavelength; so that whereas with light you can get diffraction effects from layers which are fairly close together, such as the lines on a diffraction grating, with radiation of very, very much shorter wavelength these diffraction effects are obtained from layers which are very much closer together. It is possible to get these diffraction effects from the successive layers of the carbon atoms in the molecule of a hydrocarbon. Using that tool, some extraordinary results are now being obtained at South Kensington. For example, all of us who are interested in lubrication have always held the view that a normal paraffin, made of a chain of carbon $CH_3CH_2$ groups would be a completely neutral body, and would therefore not orientate itself on to a surface in any particular way. But Professor Finch has shown that that is not the case. He has shown that the normal hydrocarbon molecules do stand up on end, just as we had thought that all fatty acids did. By incorporating a small percentage of a fatty acid into a neutral oil, we know that an increased oiliness effect is obtained; Professor Finch has found that the molecules of the fatty acid stand at a definite angle to the surface, and that they influence the hydrocarbons which normally stand up straight to take up the same orientation. This throws a new light on the subject of oiliness.

Another fascinating example refers to the fact that the liner of a cylinder fitted with an aluminium piston suffers greater wear than does the piston. The application of electron diffraction examination to the surface of the aluminium piston shows that the surface is not aluminium, but aluminium oxide (an extremely thin layer, of course). Bowden has shown that the abrasive effect of one surface on another depends not so much on the relative degrees of hardness of the material as on the melting point. That aluminium oxide has a higher melting point than iron may account partly for the effect. However, the aluminium piston is covered with a very thin layer of aluminium oxide. Nevertheless, it is remarkable that the aluminium oxide layer is partly converted into crystalline aluminium oxide in the form of the hard sapphire. In effect, therefore, the surface of an aluminium piston behaves as emery paper.

I submit that such examples of fundamental research emphasize the need for generous support for such work.

Mr. Alex. Taub: Dr. Garner refers in his introduction to the fact that for the past few years attention has been concentrated on the engine rather than on fuels—the engine still is the biggest single factor involved in the proper use of fuel. I personally think, however, that closer co-operation between the fuel man and engine manufacturer must be arranged.

One thing is certain, we should be close enough in our work in order that respective developments should not cause surprise, such as occurred in the States a year or so ago. Additional light ends were added to the fuel without notification—upsetting many of the cars with automatic chokes very seriously.

Dr. Garner has divided his remarks on fuel usage into five elements. Taking them as given in the paper:

*Easy Starting.*

He states it is difficult to separate the effect of lubricant and that of the fuel in the matter of starting. I feel this is not so. It is easy to determine when oil that is too heavy for winter use is in the sump; at least, it is easy to tell the difference when light oil is in the sump instead of heavy. Regardless of the fact that all other fundamentals may be correct, the engine may still fail to start if the drag on the rotating parts is such as to require more power than can be developed cold in one cylinder. All that is done is to kick the starter mechanism out of mesh until the combustion chamber is finally saturated with fuel—which then means you can't start at all!

There is something fundamentally wrong in the starting ability of cars in England. It obviously is not all due to incorrect lubricants. I think it fair to say that fuel development is not to blame because fuels inferior to those available here can be started in temperatures 40° lower than met with in the British Isles. Design of manifold to give fair distribution of liquid fuel is the first important step, and this is not particularly difficult to accomplish.

The first rule of importance for the fuel itself is that the carburettor at full choke must be capable of delivering a mixture-ratio equal to the demand for cold starting. Vaporization of a certain amount must occur before ignition takes place, and as vaporization drops with temperature, therefore the mixture-ratio must likewise drop.

Recognizing that mixture ratios below 8 to 1 are useless in a normal engine, the fact must be faced that mixture-ratios down to 1 to 1 are required to meet the conditions of cold starting. With flexible choke valves it is not difficult to set the carburettor to deliver the proper mixture-ratio with the manual operating button in the all-on position. As soon as the engine starts it is slipped back part way in readiness for the warm up. Of course, the least upward movement of the mixture we have to meet in the induction system, the easier the starting—this is borne out in practice.

Of course, the combustion chamber conditions may materially affect the starting. However, I believe too much importance is sometimes given to the combustion chamber and its influence on fuel burnability. One American company that has experienced difficulty in starting when the sparking plug was located over the exhaust valve refuses to consider other positions for any of its power units; therefore, all their engines incorporate cylinder-heads with sparking plugs over the intake valve in spite of the fact that their engineers have contributed much to the combustion chamber literature and have emphasized the necessity of putting the plug over the exhaust valve.

*Warm Up and Acceleration.*

Dr. Garner combines warm up and acceleration because acceleration cannot be obtained until the engine is warmed up. Yet these are two separate and distinct problems and must be handled as such. It is, of course, necessary to design a manifold with heated surfaces only at such points where the heavy ends leave the air stream. A valve in the exhaust

manifold that forces all of the exhaust up round the intake is ideal, particularly if this valve is spring-loaded so that under proper conditions, such as two thirds wide open and upwards, this valve will blow open, allowing the exhaust to follow the normal exits. If this spring-loaded valve is loaded with a bi-metal spring, then the tension of this spring varies with under-bonnet or manifold temperature. If the intake manifold is so designed as to give the minimum drop of velocity of the mixture consistent with good distribution, minimum precipitation will occur and less liquid fuel will be present in the system.

It has often been said that manifolds capable of good filling would not be good for even distribution; this is not necessarily so. We find it possible commercially to get 123 b.m.e.p. and still not sacrifice anything in the way of distribution.

Acceleration is another matter; if reasonable mixture ratios are to be employed, a mixture rich enough for accelerating through the speed range of the carburettor cannot be provided. Carburettors must have three ranges of mixture ratios—(1) for acceleration, *i.e.*, rich; (2) for full-throttle operation, *i.e.*, medium rich; (3) for part-throttle operation, *i.e.*, very lean—there should be at least two mixture ratios between (2) and (3).

The mixture ratio difference between (2) and (1) depends entirely on manifold design, sparking-plug position, gap and, most important of all, the voltage from the coil at the sparking plug.

The correct mixture can only be obtained in the carburettor by use of a throttle pump which supplies instantaneous rich mixture which usually represents an additional $1\frac{1}{2}$ to $2\frac{1}{2}$ c.c. for a period of 3 sec. With a throttle pump of this volume, it is possible to get satisfactory acceleration or flexibility with voltage up to 9,000. Without a throttle pump it might be necessary to have a voltage up to 20,000, which is beyond the break-down point of the sparking plug itself. With a combination of 14,000 voltage and a decent throttle pump and a good manifold, acceleration becomes truly a matter of power to lead ratio of the motor car. When carburettors are manufactured with greater uniformity and applied with common sense, flat spots as they are known to-day will disappear because they are the result of either low voltage or local thin mixture—or both.

*Vapour Lock.*

The motor car manufacturer has been quick to blame the fuel man for the difficulties of vapour lock, yet it is perfectly obvious that we cannot have fuel that will vaporize travelling from the carburettor to the manifold under adverse conditions of temperature and pressure without the tendency of vapour lock.

Much of the vapour lock has been caused by location of fuel pumps near the exhaust pipes and manifold or in line with hot blasts. It is interesting that the majority of the overhead-valve engines in which the fuel pump is located on the opposite side of the engine to the exhaust system have no vapour lock trouble. Of course, a certain amount of hot stalling is bound to occur under conditions of 90° F. air temperature with cars queued up four abreast, moving about half a mile in half an hour. A justifiable complaint is not being able to start after hot stalling. This has been blamed on the accumulation of fuel in the manifold which has percolated out of

the carburettor due to the heat. I have, however, time and again demonstrated to customers who are complaining of this trouble that a cupful of raw petrol can be poured through the carburettor into the manifold with the cooling water and engine condition as hot as they can be and that even so a start in 15 sec. can be obtained provided that the throttle opening is correct for starting. In other words, the most important element in hot starting is the mechanism between the starter and the carburettor for the opening of the throttle valve.

*Dilution.*

I wish Dr. Garner had given more time to the question of dilution. Crankcase ventilation is not too good to-day, and there are two reasons for this. One is a fallacious belief that the thermostat in the cooling system may interfere with cooling, but if just as much water flows through the system with as without a thermostat there can be no effect on cooling. The second reason is that the type of ventilation used would be quite satisfactory for 60 m.p.h., but is inadequate for 30 m.p.h., and most of the dilution occurs at low speeds. My experience with ventilators that are linked up to the carburettor has been that there is too much coking of the jets.

*Anti-Knock.*

Fuels to-day are more advanced for anti-knocks than engines. When combustion chambers are designed for the maximum anti-knock the compromise results in roughness and loss of fuel consumption. Volume distribution as a means for shock control has been very satisfactory. I have often wondered when the fuel man would do something with this problem of pressure rise control.

Detonation may be affected by a number of elements within the engine that are not usually considered by laboratories. For instance, it is known that detonation is a function of temperature and due to after-burning. A condition may arise which may place temperatures out of control. After-burning may be due to plug gap, or plug position, or combustion chamber. The exhaust valve and piston are over heated, and this obviously affects incoming mixtures and final temperatures and this affects detonation.

Another disconcerting item is the grouping of manufacturing variations, such as combustion chamber depth, crankcase height, connecting-rod length. These may all affect the volume of the chamber. Again, variations in the ignition distributor, camshaft driving mechanism for the distributor, looseness of chains for driving the camshaft, and variation in camshaft keyway, may all affect actual spark timing, which may vary as much as 10 deg. from standard. This is why the so-called Octane Selector should be more generally used. Admitting it is " passing the buck " to fuel men to cover a multitude of mechanical variations with a name, nevertheless, its use is necessary because fixed adjustment for initial setting is impossible.

Flywheel markings should only be used for zero setting of the Octane Selector or manual adjustment of the spark advance. Adjustment should then be made in the spark advance to fit the conditions of operation, fuel used, and mechanical variations of the engine components.

*Economy.*

Good mileage per gallon is obviously only possible through part-throttle operation, *i.e.*, range (3) quoted above. I have divided the approach to m.p.g. into two avenues, (*a*) improving the ability to burn a mixture, and (*b*) proving the burnability of the mixture. Much has been done under (*a*), such as improved distribution, proper sparking plug position, proper gaps, adequate voltage. From the work done I have found the ragged point for a given mixture ratio and a given condition of operation to be very stable—so much so that it does not appear that the same point for raggedness will be reached with every kind of fuel. There is bound to be a difference in burnability of various fuels. I feel that the fuel man should concentrate on this problem to isolate the germ of burnability and perhaps concentrate it in a blend. This may give a fuel that really *will* give more mileage—not only on the bill-posters, but actually in use!

*Lubrication.*

All agree that lights oil are overdue, the question arises are they available and how are they identified? We as engine designers should be in a position to recommend a grade of oil such as 20 or 30. Such grades should apply to any make that satisfies specification and trade names, and symbols should be used by the manufacturers of lubricants to distinguish the various features that their particular oils incorporate. This is something that is needed now—not next week or next month or next year—but *now*.

Light oils are required for ease of starting, for quick lubrication of bores and satisfactory fuel mileage. We recently demonstrated to one engineer a 12 per cent. increase in fuel mileage, between an oil equal to S.A.E. 40 as compared with an oil equal to S.A.E. 20. It is quite possible, although not desirable, to obtain mileages up to 7,000 m.p.g. with oil equivalent to S.A.E. 20—which is the lightest oil available in England to-day. From the standpoint of oil consumption with light oils this must be a matter of engine design—we cannot hope to plug up ring and bore deficiencies and gasket leaks with heavy oil.

There is some work proceeding in the States that I think our English oil engineers should investigate, namely, compounding oils to overcome ring sticking. Of course, the proper way to overcome this trouble is to keep the temperature of the rings down. Some day, and not far distant, all high-duty engines will have piston heads and ring belts oil cooled; this will not only make the rings more effective and suppress detonation, but supply the necessary oil to the bores.

Mr. E. A. Evans wrote: Nobody will quarrel with the demand for low-viscosity oil with a low pour point to facilitate easy starting in the winter. Neither does it seem unlikely that at a low viscosity, oil will reach the piston rings more rapidly than a more viscous oil after the moment of starting. Oil starvation during the first few minutes of running is admittedly all too common in promulgating wear, consequently we have an added factor in favour of low-viscosity oil. Dr. Garner emphasizes the importance of a sufficiently high-viscosity oil to meet the conditions of the piston skirt which operates at 350° F. Does the low-viscosity oil which is required for starting fulfil the requirements of the engine when it is running hard?

Before we can reply in the affirmative we must pause and think. Does the racing motorist or the air pilot use a thin oil? The answer is "No." Neither of these people is primarily interested in starting. Their job is to keep the engine running, and running well, after it has started; therefore they will use the best oil for their purpose.

These two apparently conflicting requirements lead me to ask whether we are stressing the easy starting desideratum to the disadvantage of good running conditions. In the U.S.A. we are told that thin oils meet all the conditions, therefore they use them. In this country we have not yet abandoned the medium viscosity oil for summer use. Is there a difference in design between the American and the British car to justify the two views? Until we have answered this in detail we cannot see the subject in true perspective. Let us not lose sight of the fact that the battery and the starter play an important rôle with the lubricant at the moment of starting.

Finally, before we decide to abandon a popular practice let us be quite clear that an individual consideration is not misguiding us, whether our thoughts be centred upon oil viscosity, bearing metals, or the much-discussed extreme pressure lubricants.

Mr. G. Vivian Davies wrote: The figures for petrol consumption given on page 578 of Dr. Garner's paper are very interesting. I should like to ask him if these relate to American as well as English cars, because I understand American car manufacturers claim, and I believe from inquiries I have made actually obtain, much better average consumption figures than those given in the paper, especially in the case of the larger horse-powers.

This would appear to be due partly to lighter body construction and partly to improved carburation. This is a subject where intensive research would be welcomed by the car owner if nobody else, since petrol is by far the costliest item in the running expenses of a moderate size car doing an average annual mileage.

Mr. C. G. Williams: Mr. E. A. Evans rightly stresses the necessity for consideration of all that may be involved in the use of light oils. The I.A.E. is at present studying the matter in several of its aspects.

Dr. F. H. Garner, in replying to the discussion and the written communications, wrote: Reference was made by Mr. Thornycroft to fuels for different seasons of the year, and he points out that in the early days of the automobile 680 spirit was used. Such a spirit could not be used on cars at the present day, as it would be too volatile and would lead to vapour lock, as the spirit would boil either in the carburettor jets or in its passage from the tank to the carburettor. The difference between summer and winter grade spirits, more particularly as regards warming-up qualities, can be quite easily demonstrated on a chassis dynamometer in a controlled temperature room. Mr. Thornycroft's support of low viscosity oils is very helpful, and the use of oils of flat viscosity–temperature curve, or high viscosity index, is of the greatest importance in the direction which he instances of an oil which can be used both in summer and in winter.

In Mr. Taub's interesting comments particular reference was made to the separation of the effect of lubricant from that of fuel in the matter of start-

ing. It is a matter of much greater experimental difficulty to determine the influence of fuel in starting than that of the lubricating oil: for this reason it is desirable to minimize the pronounced effect of viscosity at low temperatures as far as possible by the use of lubricating oils of very low viscosity.

Although warming-up and acceleration were discussed under the same heading, they are, in fact, treated quite separately from the point of view of the considerations involved, and, as Mr. Taub points out, acceleration cannot be obtained until the engine is warmed up.

On the question of dilution, the fact that dilution in this country does not normally exceed 3–5 per cent. would indicate that this problem is not serious in this country. I feel, therefore, that the point Mr. Taub makes as regards improvement of crankcase ventilation is a matter not so much from the point of view of dilution as of freedom from contamination of lubricating oil with undesirable oxidation products.

The general agreement that light lubricating oils are overdue for the lubrication of motor cars would undoubtedly be considerably accelerated by the adoption of a uniform scheme of grading, such as that initiated by the Society of Automotive Engineers, in which numbers—20, 30, 40, 50, etc.—have been allocated to different viscosity ranges. At present, the adoption of widely different methods of classifying motor lubricating oils, in which there is no uniformity between the designations used by different suppliers, leads to confusion in the minds of motorists which would be eliminated by the adoption of the S.A.E. scheme.

In this connexion, Mr. Evans instances the racing-car engine and the aviation engine, which in certain respects present different problems from that of the small car motor engine commonly used in this country. The important point is the use of an oil of sufficiently high viscosity to meet the temperature conditions of 350° F. prevailing on the piston skirt, and if oils of high viscosity index are used, it is possible to provide oils of quite low viscosity at ordinary temperatures and still provide satisfactory viscosity at the temperatures actually prevailing at the engine; such temperatures in the small car engine will, of course, be lower than those in the aero engines or racing engines mentioned by Mr. Evans. In this connexion, Mr. Taub refers to work carried out in the States in regard to compounded oils, and this appears to refer to a paper by C. G. A. Rosen,* who, however, instead of suggesting keeping the temperature of the rings down, actually gives illustrations of pistons which at higher temperatures gave less ring-sticking than at lower temperatures, and this was apparently due to the fact that the gumming stage was omitted. This behaviour is probably exceptional, but illustrates the inherent difficulties of the problem of ring sticking.

A further point was raised by Mr. Vivian Davies concerning the petrol consumption of American cars as against English cars, and while, of course, most American cars are of higher horse-power than English cars, evidence taken from runs on English and American cars published in *The Motor* and *The Autocar* indicates that the consumption of American cars is comparable, but may be very slightly lower than that of English cars of the same horse-power.

* *J.S.A.E.*, **40**, 1937, p. 165.

# THE DETERMINATION OF THE IGNITABILITY OF DIESEL OILS ON A LABORATORY SCALE.*

By R. Heinze and M. Marder.

The determination of the ignitability of liquid fuels in the diesel engine by means of laboratory tests has been the subject of many investigations during the last ten years. As a guide to the ignitability (cetene value), several physical constants have been taken into account, as for instance the ignition index,[1] the diesel index,[2] the viscosity–density constant,[3] the ignition value,[4] and, in conjunction with the Siedekennziffer,† the parachor [5] or the density.[6]

The views as to the applicability of the cetene values determined by means of the above-mentioned constants differ very widely.[8] Numerous commercial diesel fuels tested, when subjected to physico-chemical testing methods, yielded cetene values which corresponded well with those obtained in the testing engine. There were, however, many diesel oils of a certain origin which could not be tested by the diesel index, ignition index or viscosity–density method,[9] as, for instance, the standards cetene and α-methylnaphthalene, the sub-standards Abadan and S 300 manufactured by the Edeleanu extraction by the Anglo-Iranian Oil Company, as well as doped fuels. The reason for the occasional considerable differences between the cetene values determined by the aid of a motor and by the physico-chemical method respectively are frequently attributed to the fact that branched-chain hydrocarbons—as for instance isoparaffins—show a considerably different behaviour compared with the straight-chain hydrocarbons—as for instance *n*-paraffins—although their physical constants practically correspond.

The ignitability of doped fuels cannot be directly determined by physical methods, because the very small proportions of ignition accelerators added do not affect the physical constants of the fuels. There exists, however, a possibility of determining the ignitability of *doped* oils by testing for the content of dope addition by chemical conversion, and by adding to the cetene value of the basic fuel, determined in the usual physical way, a value corresponding to the dope content.

* Paper received July 19th, 1937.

† The "Siedekennziffer" (= *KZ*), by Wa. Ostwald,[7] forms a basis for the average boiling temperature, and thus for the average molecular weights of the compounds of which the fuel is composed. For the determination of the Siedekennziffer the oil to be tested is distilled in the distillation apparatus by Engler-Ubbelohde, and the temperatures at which 5, 15, 25, etc., up to 95 per cent. by volume are distilled over are added up, and this sum is divided by 10. Very high boiling-fuels are distilled until decomposition commences. In this case the Siedekennziffer is calculated by excluding the 5 per cent. or the 5 and 15 per cent. boiling-point temperatures from the calculation if the 95 per cent. or the 85 and 95 per cent. boiling points are not reached. If, for instance, only the 75 per cent. boiling point of a fuel is reached, to determine the Siedekennziffer the temperatures are added up at which 25, 35, 45, 55, 65 and 75 per cent. by volume distil over, and this sum is divided by 6.

Such a method assumes that the cetene value of the basic fuel, determined on the basis of physical tests, always agrees well with that determined by motor tests, and that the rise of the cetene values caused by the admixture of the dope is fixed by motor tests.

The addition of dope has in actual practice no great importance. Apart from the fact that the modern development of the diesel engine does not call for a doping even of difficultly ignitable oils,[11] the doping admixtures suggested so far, such as the peroxides, are either too expensive or unstable, or they cause, as the alkyl nitrates, deposits in the oils or corrosive damage in the cylinder and in the exhaust tubes of the engine after a short time.

Thus, first of all the question must be answered whether the ignitability of undoped diesel oils can be determined with sufficient accuracy by laboratory tests. In answering this question the following basic observations will be made.

The knowledge of one or several physical constants such as the density or also combined constants such as the ignition index, diesel index, ignition value or parachor, does not suffice to deduce from these the ignitability of diesel oils, because all these constants do not sufficiently indicate the chemical composition of the oils, which determines their behaviour in the engine. This will be understood if any one of the physical constants, as for instance the density, is, as indicated in Fig. 1, plotted for the various classes of hydrocarbons against their molecular weight. From this it can be noted that hydrocarbons with varying ignitability may possess the same density. For instance, a hydrocarbon having a density of 0·760 may be a naphthene with a molecular weight of 65, or an olefine with a molecular weight of 150, or also a paraffin with a molecular weight of 185.

For the determination of the ignitability of hydrocarbons by means of physical constants a knowledge also of the molecular weight is necessary, because the ignitability of hydrocarbons of the same class (paraffins, naphthenes, etc.) also depends on their molecular weight. The higher the latter, the greater also is their tendency to decompose and the greater is their ignitability in the diesel engine, as proved by the theory of the thermostability by Boerlage and Broeze.[12]

These observations made in connection with pure hydrocarbons are in a certain sense also adaptable to mixtures of hydrocarbons as represented by diesel oils. In this case, however, instead of the molecular weight, the average molecular weight must be taken into account, or the Siedekennziffer, which is about proportionate to the molecular weight.

A good proof of the correctness of the above remarks is formed by the test results recently published by D. J. W. Kreulen.[10] Kreulen determined the ignitability of eleven diesel oils of different origin by the single-cylinder "National" diesel engine, as well as by laboratory methods with the aid of the diesel index and of the parachor, and further by the chemical composition of the oils based on the ring analysis method.[13] From the results obtained by these methods Kreulen reaches the conclusion that the three laboratory methods applied for the tests will yield only approximate values of the ignitability, and even the diesel index method, which he considers the best laboratory test for this purpose, may show

differences up to seven cetene value units compared with the cetene value determined by the engine test.

The final conclusions reached by Kreulen are, however, based upon the erroneous assumption that in the parachor method developed by us the parachor only is applied as a basis for the ignitability. Contrary to this

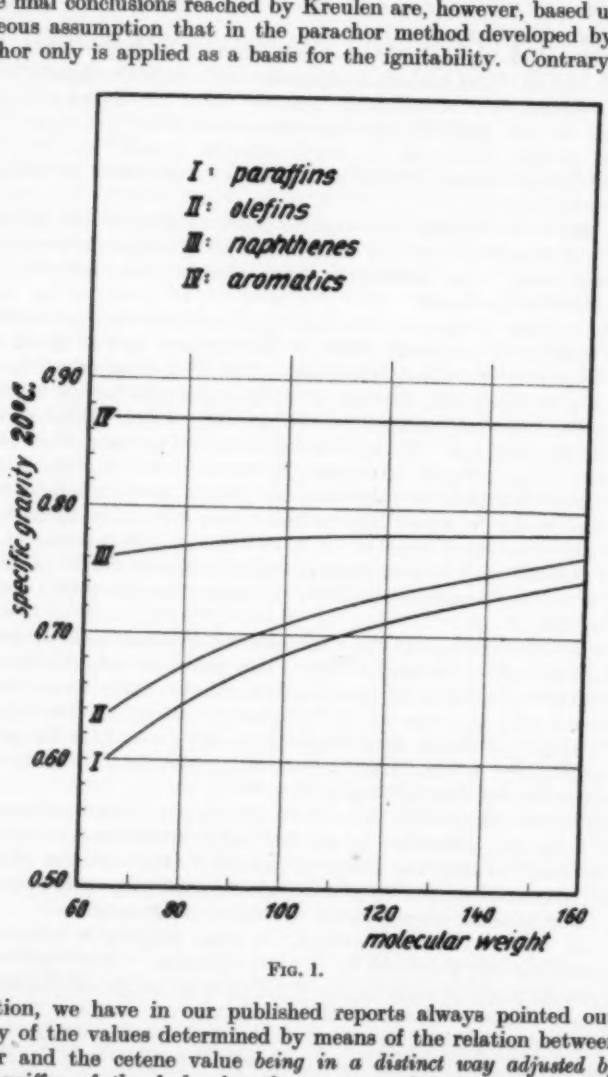


FIG. 1.

assumption, we have in our published reports always pointed out the necessity of the values determined by means of the relation between the parachor and the cetene value *being in a distinct way adjusted by the Siedekennziffer of the fuel*; for the cetene value-parachor curves are applicable to fuels of a *fixed Siedekennziffer only*. The parachor method can thus be judged only after the effect of the Siedekennziffer has been taken into account. This is effected on the basis of the empirical

observation according to which the cetene value of diesel oils having the same parachor increases with a rising Siedekennziffer by 0·3 per Siedekennziffer unit. A fixed Siedekennziffer is chosen, say about 300 as applied by us in connection with the relations which we have found experimentally; from the cetene value of those oils, which have a Siedekennziffer above this relative value (300), must be deducted 0·3 units per Siedekennziffer unit above the relative value. If diesel oils have a Siedekennziffer lower than the relative value, then 0·3 cetene number units per Siedekennziffer unit must be added to the cetene value determined by the engine. Thus, we obtain the value $CZ_{300}$ according to the equation:

$$CZ_{300} = CZ_{eng} + (300 - KZ) \cdot 0{\cdot}3.$$

$CZ_{eng}$ = cetene value determined by engine.
$KZ$ = "Siedekennziffer."

These values $CZ_{300}$ plotted against the parachor show the relation between the parachor and the cetene value as we have demonstrated in several previous articles.[14]

Example: Two diesel oils, having the same cetene value 50 determined by the engine, have the Siedekennziffer 260 and 310, whilst the corresponding results obtained by calculation from $CZ_{300}$ are equal to 62 and 47 respectively.

The cetene values determined by the engine by Kreulen have been converted to $CZ_{300}$ by calculation in the manner indicated. The calculated results are plotted against the parachor in Fig. 3. A comparison of the noticeable deviations along an average line with the values observed by Kreulen, who did not take into account the Siedekennziffer as indicated by Fig. 2, shows plainly the improvement reached by introducing the effect of the Siedekennziffer. In order to calculate the cetene value determined by the engine from the parachor-cetene value relation in Fig. 3, the value of $CZ_{300}$ is noted from the parachor corresponding to the fuel, and from this is calculated the cetene value by the engine test according to the following equation:

$$CZ_{eng} = CZ_{300} - (300 - KZ)\, 0{\cdot}3.$$

The parachor-cetene values determined without and with the Siedekennziffer are compiled in Table 1. In the first instance the average deviation between engine-tested and physico-chemically determined cetene values is equal to 4·6, and in the second case to only 1·5 cetene value units. Kreulen found by the diesel index and the ring-analysis method average deviations of 3·3 and 3·0 cetene value units (see also Fig. 2). The accuracy of the parachor method of determining the cetene value is, if the proper mode is observed, considerably greater compared with the results obtained by the diesel index or by the ring-analysis method according to Kreulen.

A further proof of the necessity of taking into account the Siedekennziffer when determining the cetene value in the laboratory is offered by the application of the results of the parachor method also to the diesel index and ring-analysis methods. In Fig. 3, besides the parachor-cetene value relation, the cetene value relation to the diesel index and to the ring analysis value $(-0{\cdot}2\,A + 0{\cdot}35\,N + 0{\cdot}85\,P)$ are also taken into

account *for diesel oils having the Siedekennziffer* 300. These relations have been obtained by applying a value of correction for the Siedekennziffer just as is applied in connection with the parachor method. Thus in the diagram of Fig. 3, contrary to the mode of operation in the methods already mentioned, not the cetene values determined by the engine

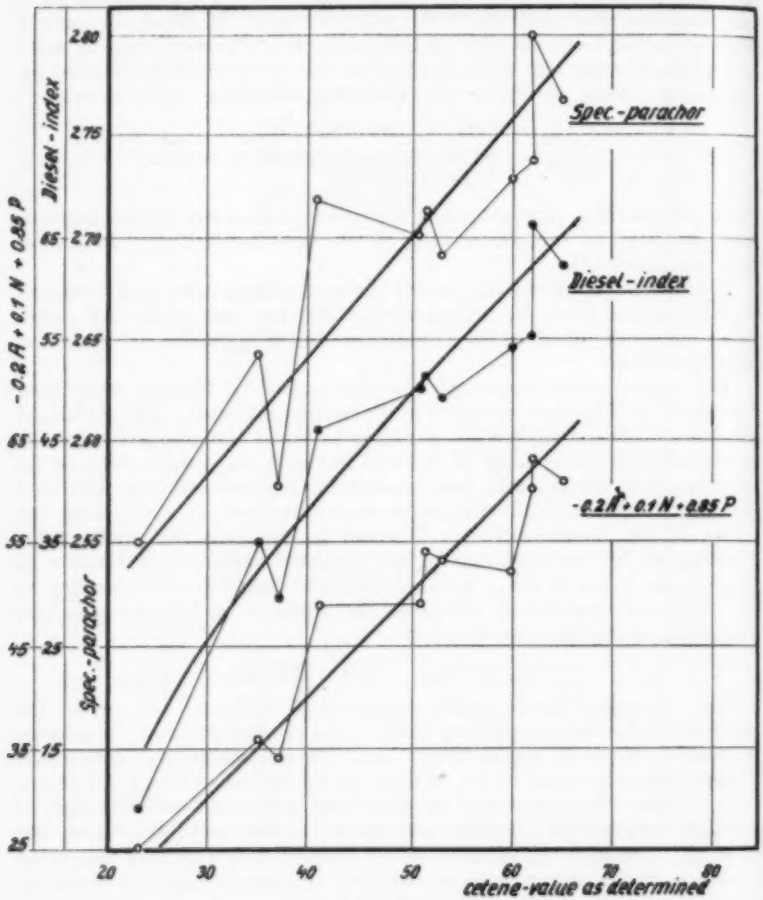


FIG. 2.

"$CZ_{eng}$" have been plotted, but the values calculated from the Siedekennziffer 300, viz. $CZ_{300}$. The calculation of this latter value was based on the equation

$$CZ_{300} = CZ_{eng} + (300 - KZ) \cdot f$$

"$f$" being a correction value which has been empirically determined,

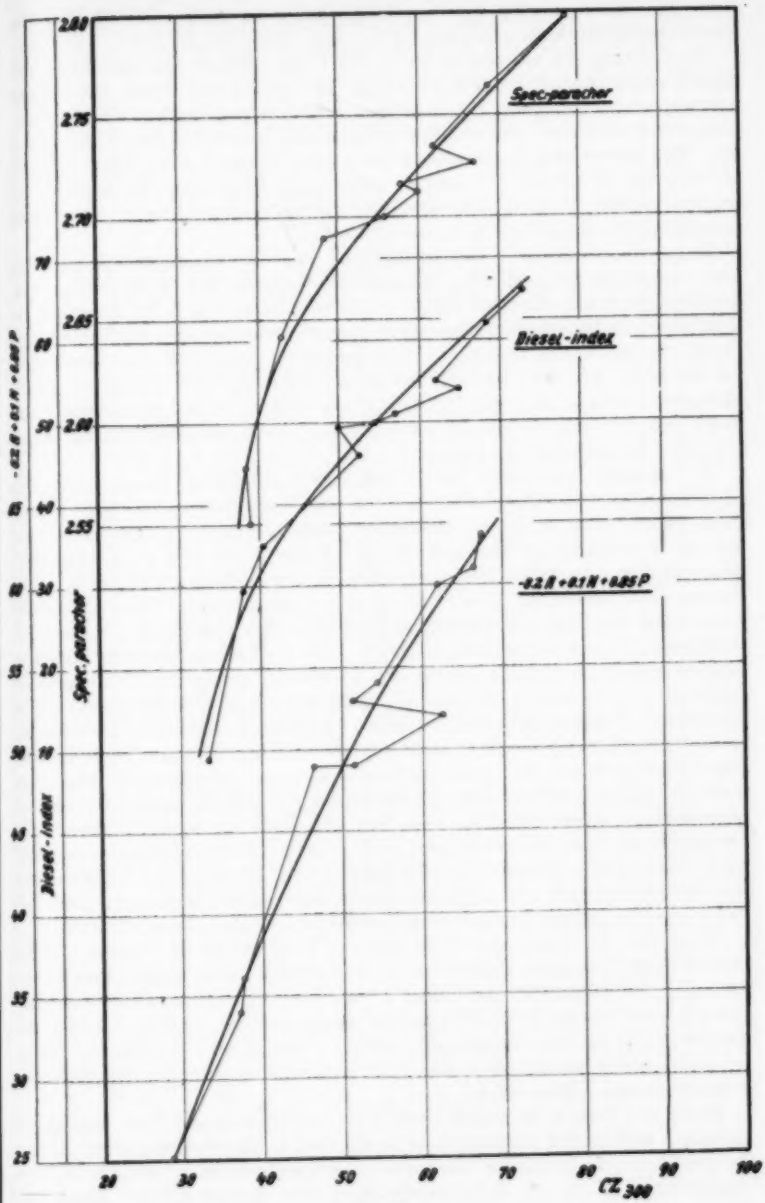
Spec.-paraffin
Diesel-index
-62 A + 0.1 N + 0.85 P
Spec. paraffin
Diesel-index
CZ 300

FIG. 3.

and was taken as 0·2 for the diesel index method and 0·1 for the ring-analysis method.

By plotting the calculated values of $CZ_{300}$ against the results of the diesel index or of the ring-analysis, the deviations from the curves introduced to indicate the average values are considerably reduced, compared with the cetene values determined by engine (see Figs. 2 and 3). The cetene values calculated from the average curves differ only by an average of 1·9 and 2·1 cetene value units from those determined by engine, whilst without consideration of the Siedekennziffer, deviations averaging 3·3 and 3·0 units have been found.

From these results it can be deduced that the discrepancies between the engine tests and the laboratory methods for determining the ignitability which Kreulen found must not, as assumed by Kreulen, be attributed to the effect of the iso-compounds which escape the laboratory methods, but to the varying average molecular weight of the components of the oils. So, for instance, the oil 4 (Table I), with regard to which Kreulen assumes that we "probably are dealing with isoparaffins," has been properly determined by all laboratory methods after having taken the Siedekennziffer into account.

As already explained in a report [15] published previously, the determination of the behaviour of the isoparaffins in the motor theoretically also causes no difficulties, since the effect of the side-chains on the ignitability of the components of the diesel oils is considerably less than on the anti-knock properties of low-boiling motor fuels. For instance, a side-chain is able to improve considerably upon the inner bond, and thus at the same time also upon the anti-knock property of hexane ($C_6H_{14}$) or of heptane ($C_7H_{16}$). The anti-knock property and the approximately reciprocal ignitability of cetane, consisting of a chain of sixteen carbon atoms, is scarcely affected by the introduction of a side-chain, because the effective range of the side-chain—for instance of a methyl group—is confined to the nearest carbon atoms. The effect of the side-chains on the ignitability of the diesel oil molecules does not become evident unless the oil molecules contain a large number of side-chains. Apart from the fact that this does not apply to diesel oils derived from crude oils or tars and to those manufactured by hydrogenation or by a synthetic process, the alterations of the physical constants caused by the introduction of a large number of side-chains are so large that the corresponding alterations of the ignitability allow for a determination.

Thus also in connection with the oil 7, of which the cetene value determined by engine differs by 5 to 6 cetene value units from those obtained by laboratory methods, it can scarcely be assumed that this discrepancy is caused by the presence of isoparaffins. In this case it must be assumed that the occasionally observed variations [16] within the range of high cetene values *by engine tests* will obscure the physico-chemical relation to the cetene value.

From the results so far discussed, it can be deduced that the diesel index as well as the parachor can be applied to the determination of the ignitability, on condition that the average molecular weight of the components of the oil is taken somehow into consideration. Since the diesel index method did not so far take into account the molecular weight

TABLE I.

*Analytical Constants and Cetene Numbers (Determined and Calculated) of Gas Oils, Investigated by Kreulen.*

| Oil. | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | 11. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Density 20/4 | 0·9310 | 0·8889 | 0·9136 | 0·8473 | 0·8522 | 0·8605 | 0·8511 | 0·8496 | 0·8168 | 0·8387 | 0·8709 |
| Mean Mol. Weight | 180 | 215 | 244 | 192 | 216 | 227 | 217 | 236 | 198 | 233 | 251 |
| Aniline Point, °C. | 7·0 | 55·1 | 54·2 | 56·6 | 65·8 | 68·9 | 70·6 | 71·6 | 72·3 | 76·0 | 72·9 |
| Surface Tension, dyne/cm. | 31·83 | 30·47 | 30·77 | 28·07 | 28·59 | 29·17 | 29·00 | 29·17 | 27·29 | 28·88 | 30·14 |
| Diesel Index | 9 | 35 | 29·5 | 46 | 51 | 50 | 54 | 55 | 66 | 62 | 49 |
| Spec. Parachor | 2,551 | 2,643 | 2,578 | 2,717 | 2,713 | 2,701 | 2,727 | 2,735 | 2,798 | 2,764 | 2,690 |
| Hydrogen | 9·73 | 12·50 | 12·01 | 12·94 | 12·92 | 12·86 | 13·04 | 12·85 | 13·57 | 13·31 | 12·51 |
| Carbon | 89·39 | 86·86 | 87·47 | 86·20 | 86·34 | 86·92 | 86·63 | 85·72 | 85·65 | 85·71 | 86·95 |
| Carbon/Hydrogen Ratio * | 9·19 | 6·95 | 7·28 | 6·66 | 6·68 | 6·76 | 6·64 | 6·67 | 6·31 | 6·44 | 6·95 |
| Calorific Value | 10,240 | 10,755 | 10,650 | 10,825 | 10,810 | 10,810 | 10,815 | 10,790 | 10,955 | 10,900 | 10,725 |
| Siedekennziffer | 249·3 | 273·4 | ~291 † | 243·0 | 272·3 | 282·7 | 275·9 | ~296 † | 245·0 | 285·9 | ~311 † |
| Cetene Value as determined | 23·5 | 35 | 37 | *41* | *51·5* | *51* | *60* | *62* | *62* | *65* | *63* |
| Cetene Value as calculated : | | | | | | | | | | | |
| (*a*) from Diesel Index | 21 | 37 | 33 | 47 | 51·5 | 50·5 | 54 | 55·5 | 65·5 | 62 | 49·5 |
| (*b*) from Ring-analysis | 25 | 36 | 34 | 49 | 54 | 49 | 52 | 60 | 63 | 61 | 53 |
| (*c*) from Parachor | 24 | 40·5 | 29 | 53 | 52 | 50·5 | 55 | 56·5 | 67 | 61·5 | 48·5 |
| (*d*) from Parachor and Siedekennziffer | 22 | *36* | *36* | *41* | *49* | *49·5* | *54* | *61·5* | *62* | *66* | *55·5* |
| (*e*) from Diesel index and Siedekennziffer | 22 | 36·5 | 37 | 39 | 50 | 51 | 53·5 | 59 | 61 | 64 | 55·5 |
| (*f*) from Ring-analysis and Siedekennziffer | 23·5 | 35 | 36 | 44·5 | 52·5 | 48·5 | 50·5 | 63 | 62·5 | 63·5 | 55·5 |
| (*g*) from Density 20/4 and Siedekennziffer | 21 | 36 | 37 | 44 | 53 | 51·5 | 55 | 62 | 62 | 65 | 55 |

* Derived from the carbon and hydrogen contents determined by Kreulen.

† The Siedekennziffer of these oils was not determined by Kreulen; therefore, instead of the Siedekennziffer, the 50 per cent. boiling point was used.

of the components of the fuel, this will explain the many discrepancies between the cetane values determined by diesel index and engine.

Also the ring-analysis values deduced by Kreulen $-0{\cdot}2\,A + 0{\cdot}1\,N + 0{\cdot}85\,P$ permit a correct determination of the cetene values if the average molecular weight or the Siedekennziffer of the oils is taken into account. Although the cetene values obtained by the ring-analysis method (see Table I) still show larger differences from the cetene values tested by engine than the parachor and diesel index cetene values, it can be expected that, owing to the further improvement of the ring-analysis method by Waterman, Vlugter and van Westen, by this method better results in determining cetene values will be obtained.

The possibilities of determining the ignitability by laboratory methods are by no means exhausted. Just like the data already mentioned, a large number of other physical and chemical data, which have been investigated as to their relation to the cetene value and are described elsewhere,[17] may be taken into account for determining the ignitability. Applicable for the determination of the cetene value are the *density, refractive index, gross and nett calorific value, carbon and hydrogen content, carbon–hydrogen ratio, aniline-point, viscosity and viscosity–density constant.* With all these constants the effect of the *average molecular weight on the ignitability of the oils must be taken into consideration.*

After these remarks it is immaterial which constant is applied apart from the Siedekennziffer for determining the cetene value by the laboratory method. In order to render the method of determination as simple and exact as possible, it is best to choose a constant which can be easily determined and which gives the largest range of variations for oils with varying ignitability. Under this consideration the *density* appears to be particularly suitable for testing the ignitability.

To prove the adaptability of the density (in connection with the Siedekennziffer) for the determination of the cetene value, altogether 216 diesel oils of widely varying origin have been tested in the C.F.R. motor as well as by the laboratory method on the basis of density and Siedekennziffer.[18] Apart from oils of uniform origin such as diesel oils from crude oil, lignite tar, coal tar, and shale oil as well as those manufactured by hydrogenation, synthesis or extraction, mixtures of oils of varying origin have also been tested, as for instance mixtures from lignite tar oil and synthetically recovered oils. Several oils were divided up into a number of fractions, and of these the cetene value was determined individually. The hydrocarbons used as a standard testing basis, viz. cetene and α-methylnaphthalene, have also been tested in this connection as well as the sub-standards Abadan and S 300 of the Anglo-Iranian Oil Co., which are used by many testing stations.

The laboratory test was carried out in the following manner:

From the density–cetene value curve as plotted in Fig. 4 the calculated value of $CZ_{300}$ is read off for the density of the oil to be tested and substituted in the equation:

$$CZ_{eng} = CZ_{300} - (300 - KZ)\,.\,f.$$

In this equation $CZ_{eng}$ stands for the required cetene value obtained

by the C.F.R. motor, $KZ$ for the Siedekennziffer and $f$ for a correction value depending on the Siedekennziffer as follows:

| $KZ$. | $f$. |
|---|---|
| 200 | 0·40 |
| 250 | 0·35 |
| 300 | 0·30 |
| 350 | 0·25 |

With an increase of the Siedekennziffer the $f$ value falls by 0·01 * for every 10 Siedekennziffer units.

The results of this work [18] published recently show in all instances a good conformity between the cetene values determined by engine and those obtained by the density–Siedekennziffer method. Only within the range of high cetene values (above 60) considerable discrepancies (up to 5 units) have been found between the density–cetene values and those determined by engine. These discrepancies can be fully explained by a peculiarity of the engine-test determination of the ignitability with the aid of standard test oils. This peculiarity is that, in connection with oils having a high ignitability, the engine requires operating conditions calling for too great an exactness to obtain reliable cetene values (see original report). Fig. 4, in which the calculated values of $CZ_{300}$ are plotted for 145 diesel oils of different origin, reflects the exactness of the density method. The deviations from the line drawn as an average directly represent the differences between the cetene values determined by engine test and by the density method respectively.

The reliability of the density method for the determination of the cetene value can therefore not be doubted, and it can also be expected that the cetene values which Kreulen obtained from eleven diesel oils tested in the National single-cylinder engine can be plotted against the density in the same manner as the C.F.R. cetene values, and that they will also represent a reliable cetene value–density relation.

Fig. 5 indicates that the ignitability determined by means of the National motor can be also ascertained by means of density and Siedekennziffer. The discrepancies of the $CZ_{300}$ values around the average line in Fig. 5 are even smaller than those obtained by any other laboratory methods. The average difference between the cetene values determined by the National single-cylinder engine and those taken from the curve of Fig. 5, calculated for the corresponding Siedekennziffer, amounts to only 1·5 cetene value units.

The density method is thus reliable in every respect for the determination of the ignitability of diesel fuels. For this reason, and on account of its simplicity, it deserves the preference given to it in comparison with other methods, details of which have been published in the technical literature. Since, for the determination of the density–cetene value, it quite suffices to measure the density up to the third decimal point, it is possible to determine it for obtaining the calculated value of $CZ_{300}$ by means of an

* For commercial diesel oils with a Siedekennziffer between 260 and 310 it generally suffices to use the constant correction value 0·3, whilst with oils with a particularly low or high Siedekennziffer the above-mentioned flexible factor has proved to be more suitable.

*areometer*, and, based on the relation between $CZ_{300}$ and the density, an areometer can be devised [19] which, instead of indicating the density, shows

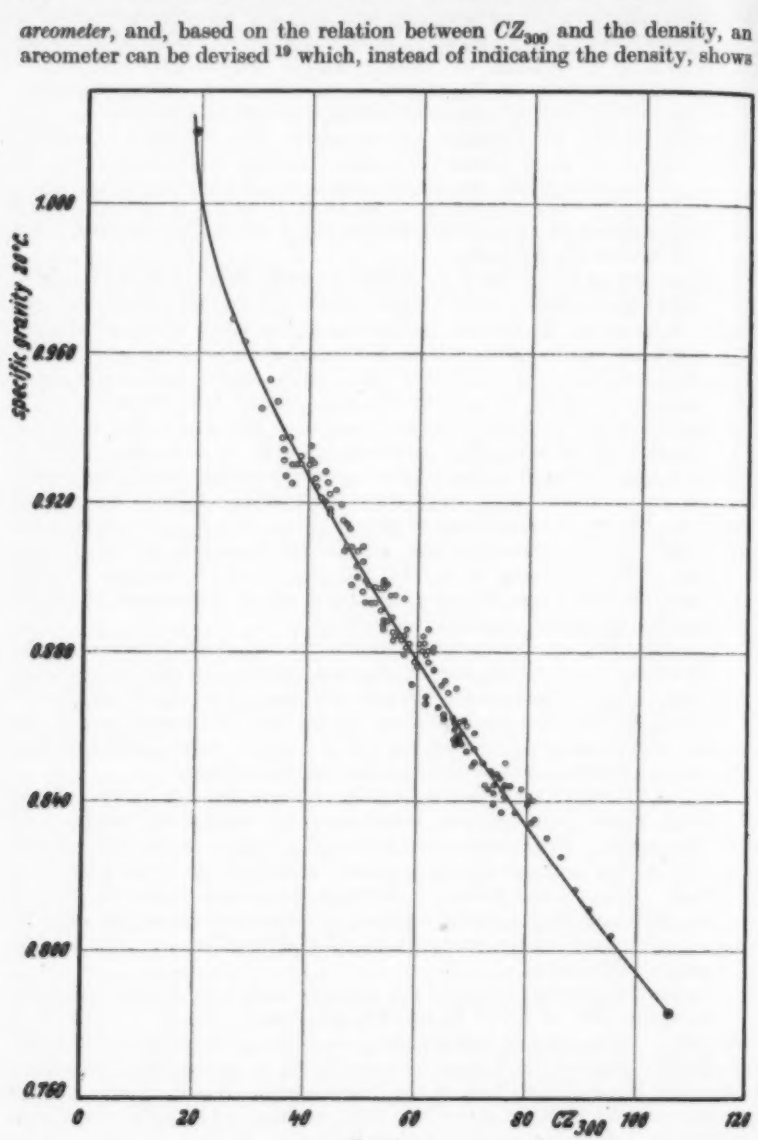


FIG. 4.

on its scale figures representing the calculated value of $CZ_{300}$. By means of such an areometer the determination of the cetene value becomes very simple indeed.

By immersing these so-called cetene value areometers into the oil to be tested, the indicated calculated value of $CZ_{300}$ is noted, and from this the real cetene value of the oil is deduced by calculation :

$$CZ_{eng} = CZ_{300} - (300 - KZ) \,.\, f.$$

For $f$, the factor depending on the Siedekennziffer is applied, which

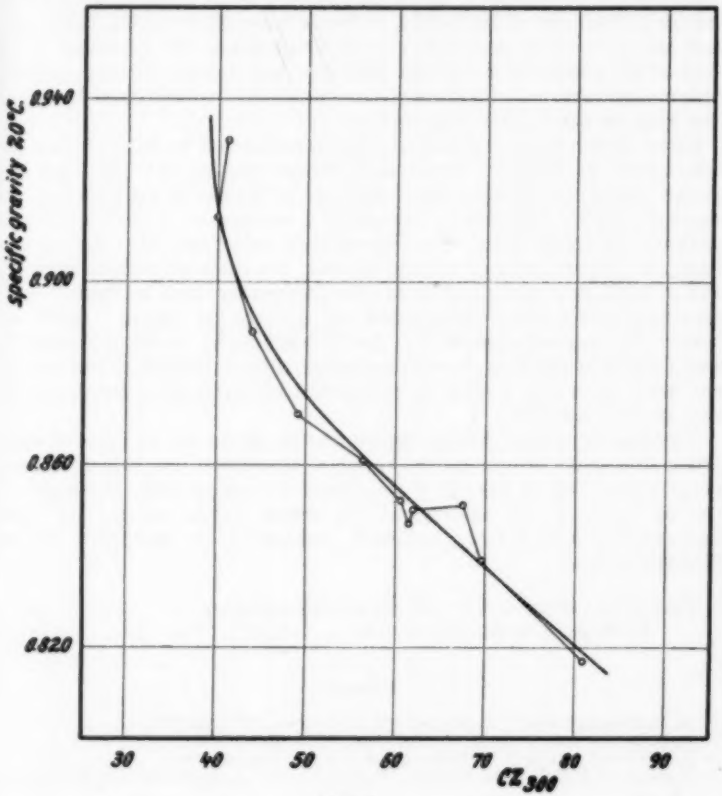


FIG. 5.

gives the most favourable results in determining the cetene value based on the density.

The method described has not only proved its reliability in testing numerous diesel oils of practically any origin, but it has also assisted in carrying out the technical manufacture of diesel oils from tars of any kind in such a way that diesel oils are recovered which are of the best possible quality, and which also meet the requirements of the high-speed diesel engine.[20]

SUMMARY.

In several recently published articles the reliability of the laboratory methods for determining the ignitability of diesel oils has been repudiated. In spite of these efforts it has been proved by the above report that, by the proper application of the parachor or density method developed by the authors, cetene values well comparable with those determined by engine tests are obtained. Standard as well as sub-standard testing oils, and also diesel oils of any origin, as for instance from crudes, lignite tar, coal tar or those manufactured by hydrogenation, by synthesis or by extraction, when tested by the parachor and density method, yielded within very narrow limits the same cetene values as determined by engine test with the aid of the C.F.R. motor.

Based on the analytical and physical constants of the eleven diesel oils determined by Kreulen, it has been further proved that well agreeing cetene values can be determined not only by means of the parachor and density methods, but also by the aid of numerous other constants, as for instance the diesel index, the ring-analysis value and also the calorific value, the hydrogen and carbon content, the ratio of carbon–hydrogen and so forth, and cetene values can be obtained by these methods in good agreement with those determined in the testing engine. However, besides the constants mentioned, the Siedekennziffer of the diesel oils has also a material effect on the determination of the ignitability, and this has not been taken into account in connection with the diesel index and the ring-analysis method.

The density method for the determination of the cetene value of diesel oils undoubtedly represents the simplest laboratory test, which is lately being carried out by the aid of the so-called "cetene value areometer."* On the scale of this instrument the cetene values of the oils under investigation are directly indicated, subject to a correction for the Siedekennziffer.

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# PETROLEUM WAX: DETERMINATION, ANALYSIS, AND CONCLUSIONS ABOUT ITS COMPOSITION.*

By D. S. McKittrick, H. J. Henriques and H. I. Wolff.†

SUMMARY.

A method of determining the wax content of oil and the oil content of wax has been developed that appears to be more accurate and reproducible and of much wider applicability than any previously published. The wax is crystallized from ethylene dichloride at − 35° C. or from chloroform at − 55° C.

The determination of melting-point and refractive-index distributions of the different waxes in a mixture, separated by stepwise crystallization at successively lower temperatures, is a useful way of characterizing the wax.

Low-melting waxes, which must be removed to produce oils of low pour-point, have been found in oils together with the expected high-melting ones. High-melting fractions of *distillate* waxes contain large proportions of normal paraffins. In fractions with successively lower melting points, isoparaffins, naphthenes, and probably also aromatics, in that order, may predominate. The higher-melting fractions of *residue* waxes are not predominantly normal paraffins, but contain also large proportions of hydrocarbons of other series. Although American crudes, Eastern, Mid Continent and Western, differ considerably, the compositions of the waxes from the *distillates* from the three types are very similar. The waxes from the *residues*, however, differ, showing characters related to those of the parent crudes.

Petrolatums have been shown to be mixtures of moderately hard waxes with oils of low pour-point.

## PART I.—THE DETERMINATION AND ANALYSIS OF WAX.

### A. Introduction.

While the need of routine methods for wax determination as an aid in evaluating the newer dewaxing processes and as a research tool for broadening the general knowledge of petroleum is increasing, all known methods have more or less serious shortcomings.[1] The Holde method [2] has been shown to give a measure of the *solid* wax suspended in the oil at about 20° C., with no indication of the amount of higher- and lower-melting waxes still in solution.[2a] The press method is inapplicable. The method of Wyant and Marsh,[3] a variant of the Holde method using acetone at 60° F., and that of Henderson and Ferris,[4] using nitrobenzene, are unsatisfactory for waxes of low oil content. The method of Wilson and Wilkin [5] using ethylene dichloride at 0° F. gives a partial separation of oil and wax, the wax content being determined from the refractive index of the wax fraction and a reference curve. This method is satisfactory for control work in which all samples have the same origin. The somewhat similar method of Diggs and Buchler [6] is also suited to routine work.

To overcome the limitations of these methods, the procedure here described—crystallization from ethylene dichloride at − 35° C. or from

* Paper received September 16th, 1937.
† Shell Development Company, Emeryville, California.

chloroform at — 55° C.—was developed. It is applicable to residues or distillates from all types of crudes, and does not appear to be sensitive to the presence of asphalt. It may be used to determine either wax in oil or oil in wax, and has given consistent results in the hands of a number of operators. In the same apparatus a fractional crystallization of a wax sample can be made that permits some useful conclusions about its composition, what is hereafter called the characterization of the wax.

### B. Method.

A single crystallization at — 35° C. from ethylene dichloride (or at — 55° C. from chloroform) suffices when only the proportion, not the characteristics, of the wax is desired, as in the determination of wax in oil or oil in wax. The material soluble at — 35° C. or — 55° C. is taken as wax-free oil; the insoluble material is reported as wax. It should be borne in mind that the terms wax and oil are used throughout this report in accordance with these definitions. For characterization the wax is crystallized and filtered from a solution of ethylene dichloride or chloroform in a stepwise manner at successively lower temperatures that are governed by the nature of the sample; the yield, melting range and refractive index of each fraction are determined.

1. *Choice of Solvent.* A satisfactory solvent for this work must be a good solvent for the oil and a very poor solvent for the wax at the temperature of the final crystallization, must not freeze at that temperature, and must be of such a nature that a clean mechanical separation of solvent and wax is possible. The preferred solvent, ethylene dichloride, has the desired properties to a marked degree, and its low boiling point permits its easy removal. The pure compound freezes at — 35·3° C. Certain highly paraffinic oils are not, however, sufficiently soluble in ethylene dichloride; for them chloroform is suitable, if the final crystallization is made at — 55° C. instead of at — 35° C. Pure solvents were used in all the experiments reported here. There is obviously a limit to the proportion of impurities that can be tolerated without the results being affected.

2. *Apparatus.* The apparatus used, shown in Fig. 1, permits cooling and filtering oil : wax : solvent solutions without transferring them to a second vessel. The cylinder (*A*) is a Pyrex tube about 18 cm. long and of such diameter that it is a loose fit in the 4-cm. Büchner funnel (*B*). The lower end is ground plane to seat on a filter-paper. The upper end is closed with a flat rubber disk faced with lead foil to prevent leaching of the rubber by the solvent, and held in place by the spring fastening shown, which is of a type commonly used on food and beverage bottles. The Pyrex tube and Büchner funnel are connected with a short piece of thick rubber tubing (*C*) or suitably cut rubber stopper, which serves to make the joint fluid-tight. The receiver (*D*) is a 200-ml. balloon flask fitted with a vacuum connection.

3. *Operation.* The cooling cylinder with the rubber connector in place is supported with the small end down and closed, and the waxy material and 75 ml. of solvent are introduced. Samples of 1 to 2 g. of waxy oil or of about 0·5 g. of oily wax are the most convenient. The Büchner

funnel with filter paper in place and the receiver with a length of suction tubing are attached to the cooling cylinder as shown, and the whole is warmed in a bath to ensure solution of the wax. If dirt or other foreign material is present, it is removed by filtration at such a temperature that all soluble material is in solution. Filtration is accomplished by inverting the apparatus, removing the cap at (*A*), and applying vacuum to the receiver. The clarifying filtration completed, the filtrate is poured back into the cooling cylinder, a fresh filter-paper inserted, and the apparatus reassembled. The whole, cap down and balloon flask up, is immersed to above the Büchner funnel in acetone contained in a wide-mouthed 1-gallon

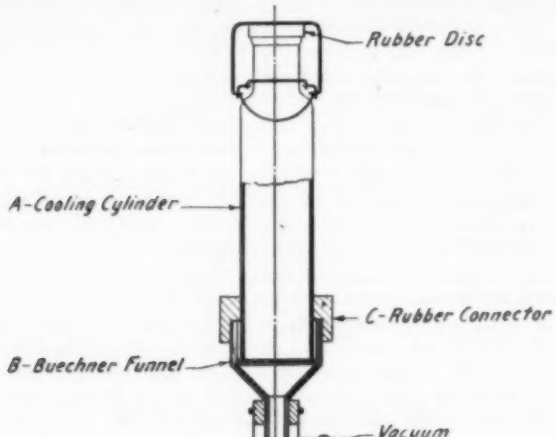



FIG. 1.

FRACTIONAL CRYSTALLIZATION APPARATUS.

Dewar vessel. It is held ½ to ¾ hour at each temperature, which is controlled by the addition of solid $CO_2$. If only the proportion of total wax or oil is desired, one filtration at the minimum temperature followed by a 25 ml. wash of chilled solvent suffices.

The initial temperature of the fractional crystallization is dependent on the oil content and the melting point of the hardest wax present, and has varied in the materials analyzed from + 40° C. to − 20° C. The selection of each lower temperature is guided by the size of the wax cake, care being taken to make each fraction from 5 to 10% of the original sample. The final fraction is always crystallized at − 35° C. from ethylene dichloride or at − 55° C. from chloroform.

After each filtration the apparatus is removed from the Dewar vessel and wiped free of acetone; the Büchner funnel is disconnected from the flask, and the wax cake washed with hot hexane (or petroleum ether) into a tared 50-ml. beaker. Care is taken to wash the wax remaining on the sides of the cooling cylinder into the beaker. The cylinder is disconnected from the funnel and capped, and the filtrate from the balloon flask transferred to it. The apparatus is then reassembled in the cooling position and placed in the acetone, which has been cooled to the next lower temperature. The hexane and remaining solvent are removed from the wax by evaporation, and the fraction is weighed.

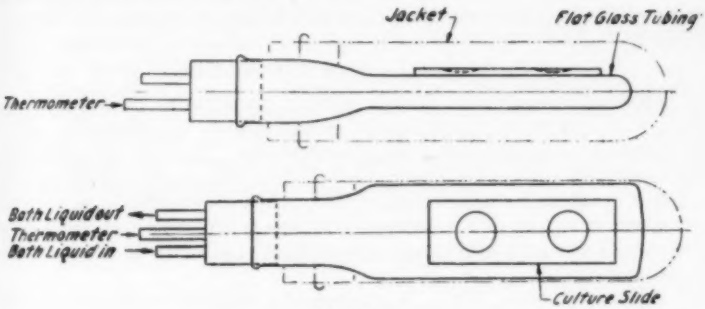



FIG. 1a.

SETPOINT APPARATUS.

In the determination of wax in oils or of oil in waxes, the percentage is based on the weight of the wax and of the initial sample. In characterization, the percentage of each fraction is determined from its weight and from the weight of all the fractions; the discrepancy between the total weight and the initial weight of the sample is apportioned among the several steps. This difference is small, amounting to 4 per cent. or less.

4. *Properties of Fractions.* The melting ranges are determined under the micropscope using a controlled-temperature stage and polarized light. The procedure gives a range large in comparison with the A.S.T.M. melting point, which, however, cannot be used even if desirable because it requires a large sample.*

The refractive index is determined with an Abbé refractometer, at 90° C. to ensure homogeneity of the sample.

The amount of oil in the soluble portion from a fractional crystallization is always too small (less than 1 ml.) for an A.S.T.M. pour-point determination. The reported temperature, which is *not* a melting point, has been called the set-point, and is determined with the apparatus shown in Fig. 1*a*. The standard culture slide (1 × 3 in. with 1·75 mm. depressions) is cemented with Canada Balsam to the flat tubing through which the bath liquid circulates. The insulating jacket contains a few lumps of calcium chloride to prevent condensation. Into each of the depressions

* It was found with a number of samples that the mid-point of the melting range was within about 1° C. of the A.S.T.M. melting point.

0·05 c.c. of oil is measured from a 1-c.c. hypodermic syringe graduated to 0·01 c.c., the jacket is put in place, and the assembled apparatus is supported with the slide flat. The samples are heated to 115° F., and then cooled to 70° F. during 15 minutes. The cooling rate from 70 to 20° F. should not be more than 2° F. per minute and below 20° F. not more than 1° F. per minute. Every 2½° F., starting at a temperature about 10° F. higher than the expected set-point, the apparatus is rotated a quarter turn about its long axis and the sample is observed. The highest temperature at which the sample refuses to flow in five seconds is reported as the set-point. Experiments with a number of oils of known pour-point show that the set-points of residues are about 12½° F. higher and those of distillates about 5° F. lower than their A.S.T.M. pour-points.

### C. Adaptability of the Method.

1. *Effect of Temperature.* Although it is desirable to control the temperature of the final crystallization rather closely, no elaborate devices are necessary, manual control being satisfactory. Too low a temperature may cause the solvent to freeze; too high a temperature will certainly lead to low values for wax, because the amount crystallized is less. Since the definition of wax on a melting-point basis is arbitrary and small errors in manipulation may also enter, temperature control to ½° C. appears to be satisfactory.

2. *Effect of Dilution Ratio.* No systematic attempt was made to determine the range of dilutions that can be used, because it probably varies with the oil. Wax determinations on a number of samples of different oils gave good results with dilutions ranging from about 40 to 100 ml. of ethylene dichloride to 1 g. of oil. The greatest difference between results was 3·5 per cent. of the mean wax content, or a deviation from the mean of 1·8 per cent. The approximately average dilution, 75 ml. to 1 g., is satisfactory, in that the volume is not excessive and the amount of oil adhering to the wax cake is negligible.

3. *Effect of Asphalt.* The determination of wax in oil with ethylene dichloride is not much affected by the presence of even considerable proportions of asphalt, except that filtration rates are decreased. It has been found in one case that only a negligible amount, 4·26 per cent., of a sample of asphalt * was insoluble in ethylene dichloride. As a check on the method, a sample of Ventura (California) Residue was deasphaltized with butane to yield 82 per cent. of oil, the wax content of which was determined with ethylene dichloride as 14·5 per cent., or when referred to the original residue, 11·8 per cent. This compares favourably with the results with two samples of the original residue, which were 11·2 and 11·6 per cent. Experiments on the effect of various proportions of asphalt (up to 20 per cent.) added to a deasphaltized oil showed that the differences are probably within the limits of accuracy of the method, being in all cases less than 10 per cent. of the wax content.

4. *Freedom of Wax Fractions from Oil Contamination.* To determine whether or not the melting ranges of the wax fractions were really repre-

* Prepared from Coalinga residue and equal to about 10 per cent. of the residue.

sentative, a large batch of crude wax * was split by crystallization from ethylene dichloride into seven wax fractions and an oil, soluble at − 35° C., having a pour-point of approximately − 20° C.† Each of the seven wax fractions was again fractionally crystallized from ethylene dichloride. The data obtained are presented in Fig. 2. The refractionation extended the melting range of each of the original fractions, and in each case a small amount of oil was separated, as is shown in Fig. 2 by the smaller cross-hatched areas somewhat removed from the main area of the fraction. The scale of the figure does not permit a fair estimate of the size of these areas. The total of all the material soluble at − 35° C. (oil) in the seven refractionations was less than 2·6 per cent. of the original wax, or an average of about 0·4 per cent. in each of the fractions, proof that a very good separation is obtained and that the effect of oil retained in the wax fractions is negligible.

5. *Reproducibility and Accuracy.* To test the reproducibility of the determination of the wax content of an oil by a single crystallization from ethylene dichloride at − 35° C., duplicate analyses were made with four oils. The results, given in Table I, agree within 0·5 per cent. of the total sample, or within 5 per cent. of the wax present.

TABLE I

*Duplicate Wax Determinations.*

| Sample. | Ref. | Percentage of Wax. | | Difference, per cent. | Difference as per cent. of deter. value. |
|---|---|---|---|---|---|
| | | First deter. | Second deter. | | |
| Ventura Distillate DA . | 1 | 16·8 | 17·3 | 0·5 | 2·9 |
| Ventura Distillate #2 . | 2 | 13·7 | 13·4 | 0·3 | 2·2 |
| DW 175 . . . . | 3 | 8·1 | 8·5 | 0·4 | 4·8 |
| Filtered Ventura Distillate | 4 | 14·5 | 15·0 | 0·5 | 3·4 |

1. Sixty-one per cent. overhead from Ventura Residue DA, redistilled with steam. "DA" is a convenient abbreviation of "deasphaltized."

2. Ventura Distillate #2 is a cut from 24 to 59 per cent. from asphaltic Ventura Residue, redistilled with steam.

3. Ventura Distillate DA partially dewaxed, 91 per cent. yield. "DW" stands for "dewaxed."

4. Obtained from Ventura Distillate by filtering without solvent under 30 lb. pressure at room temperature. Pour-point = 60° F.

The oil samples were all of about the same size, but had, as the table shows, very different wax contents. In all the determinations, however, the differences in duplicate determinations were a nearly constant fraction of the original sample, and did not vary with the wax content; it appears, therefore, that with samples of increasing wax content the percentage differences of wax found in duplicate determinations will always decrease.

* Precipitated from Ventura Distillate in 8 volumes of *iso*pentane at − 20° C., and further "deoiled" with 5 volumes of acetone at − 20° C. Melting range 28–50° C., $n_D^{20}$ 1·453.

† The pour-point was determined by the A.S.T.M. procedure except that only 20 ml. of oil was used instead of the 40 ml. required.

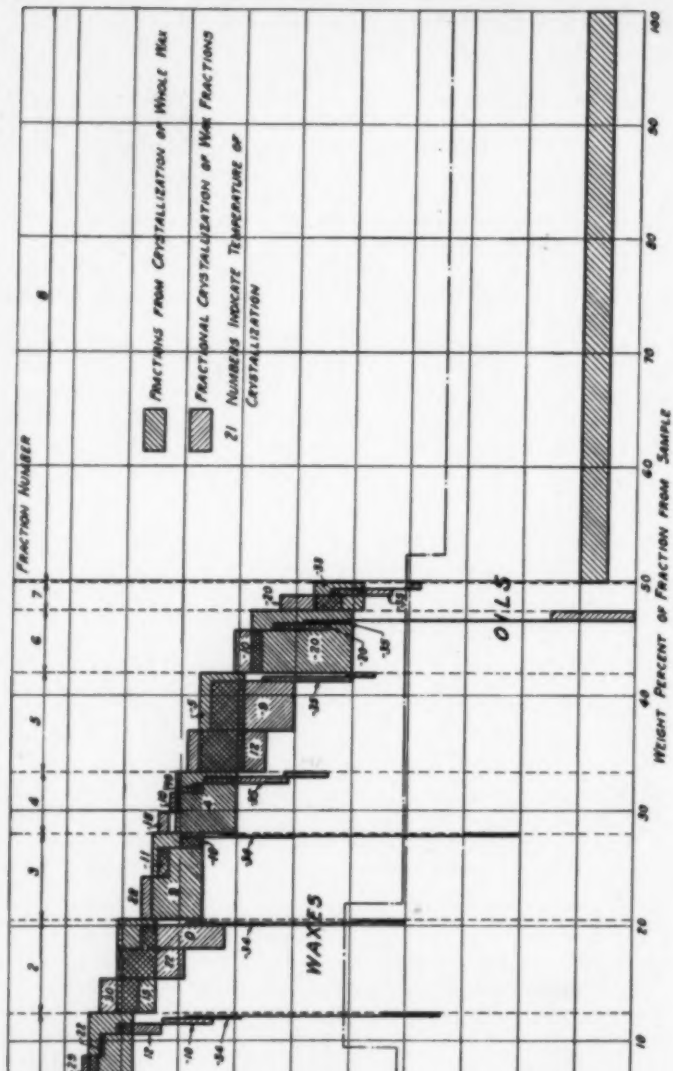

FRACTIONS FROM CRYSTALLIZATION OF WHOLE WAX
FRACTIONAL CRYSTALLIZATION OF WAX FRACTIONS
21 NUMBERS INDICATE TEMPERATURE OF CRYSTALLIZATION
FRACTION NUMBER
WAXES
OILS
MELTING RANGE OF FRACTION °C
WEIGHT PERCENT OF FRACTION FROM SAMPLE

FIG. 2.

FRACTIONAL RECRYSTALLIZATION OF VENTURA DISTILLATE WAX.

To determine the effect of the wax content on the accuracy of the determination, oils of different wax contents were blended and the wax contents of the blends determined. The magnitude of the differences between the observed and calculated wax contents of the two blends was independent of the proportion of wax present. The error is probably constant, and the percentage difference might be expected to be less for samples of higher wax content. The results on samples containing about 5 per cent. wax indicate a reliability within 0·3 per cent. of the original sample or within 10 per cent. of the wax present.

### D. Comparison of Fractional Crystallization from Ethylene Dichloride with the Holde Method.

Since the Holde method is considered the standard for the determination of wax, any method proposed to replace it should, of course, be demonstrably superior. Comparisons on three bases are made in the following sections.

1. *Difference in the Waxes Separated by the Two Methods.* A sample of an Iraq raffinate was found by the Holde method to contain 21·9 per cent. of a wax melting from 40° to 61° C. The filtrate from this determination was freed of solvent, and the oil filtered with ethylene dichloride at − 35° C. to give an additional 8·4 per cent. of wax melting from 21° to 25° C. The ethylene dichloride method used directly gave 29·9 per cent. of wax melting from 37° to 58° C. The single crystallization at − 35° C. gave a proportion of wax almost exactly equal to the sum of the proportions by the other two determinations, a good indication that the nature of the waxes separated by the two methods is the same, and that crystallization from ethylene dichloride separates additional low-melting fractions. It is of interest that the 8·4 per cent. of wax melting from 21° to 25° C., though it was 28 per cent. of the total wax, only lowered the melting range of the whole wax 3° C. (40–61° C. to 37–58° C.), clear evidence of the formation of solid solutions. The important fact in this comparison is that the crystallization furnishes a measure of the low-melting waxes, whereas the Holde method does not. Since it has been shown that the removal of low-melting as well as high-melting waxes is essential if oils of low pour-point are to be produced, it is clearly desirable to have a method for determining the amount of these waxes.

2. *Determination of Wax in a Number of Oils of Different Character.* Table II presents a comparison of the results of wax determinations by both methods on a number of oils.

The Holde method was not usable with two of the oils, both residues. This is to be expected, since the initial step in the Holde method is the distillation of the sample, which involves the almost certain thermal decomposition of a portion of the sample and a possibility that the heavier, less volatile waxes may not distil. Since one of the residues had been deasphaltized, the failure of the Holde method here is not due to the presence of asphalt. In most cases the fractional crystallization gave rather higher values than the Holde method. Neither method could be used with Pennsylvania Bright Stock, which is not soluble in either solvent; chloroform is, however, satisfactory.



FIG. 2.
FRACTIONAL RECRYSTALLIZATION OF VENTURA DISTILLATE WAX.

TABLE II.

*Comparison of Wax Determinations by Crystallization from Ethylene Dichloride and by the Holde Method.*

| Waxy oil used. | Ref. | Percentage of Wax. | |
|---|---|---|---|
| | | Crystallization from ethylene dichloride. | Holde method. |
| Ventura Residue | | 11·2, 11·6 | Not filterable owing to asphalt |
| Ventura Distillate | | 14·0 | 11·9 |
| Mid-Continent Residue DA | | 16·6 | 33 * |
| Mid-Continent Residue DA/DW | | 3·6, 3·6 | No result * |
| Mid-Continent Distillate | 1. | 13·4, 13·6 | 12·6 |
| Iraq Raffinate | 2. | 29·9, 29·9 | 21·8, 21·9 |
| Black Bayou (Gulf Coast) Raffinate | 2. | 5·8, 6·2 | 4·1 |

*. Separation of oil and solvent make Holde method unusable with these oils.
1. Prepared in this laboratory by vacuum distillation.
2. Prepared by fractional extraction.

3. *Effect of Asphalt on Wax Determination.* Asphalt to the extent of 2 per cent. by weight of the sample did not appreciably alter the results with either method. The presence of 10 per cent. or more of asphalt made filtration impossible in the Holde method, and slowed it down considerably in the case of ethylene dichloride, but fairly accurate values for the wax content could still be obtained with the latter.

## E. CHLOROFORM AS A SUBSTITUTE FOR ETHYLENE DICHLORIDE.

Ethylene dichloride is unpractical for very paraffinic oils. Attempts were made to increase its solvent power by the addition of hydrocarbons such as toluene and *iso*octane. Although toluene was the best of the diluents, none of the mixtures of ethylene dichloride and hydrocarbon was satisfactory. Other pure solvents were tried, and chloroform was finally chosen. The number of solvents with the proper range of solvent properties is rather small: trichlorethylene, for example, dissolves too much of the wax, propylene dichloride does not dissolve the oil. The following discussion considers the usefulness for three purposes of the better solvents: (1) ethylene dichloride, (2) an equi-volume mixture of ethylene dichloride and toluene, and (3) chloroform.

1. *Determination of Wax in Oil.* This determination is somewhat more sensitive to choice of solvent than the characterization of the wax, because the oil content of the sample is higher and there is a greater tendency for the solution to separate into two liquid phases. Eight experiments were made with the above three solvents and four oils, two of which were not miscible with ethylene dichloride at — 35° C., yielding the data in Table III. The results with Pennsylvania Distillate show that chloroform at — 55° C. gives very nearly the same figure for wax as does ethylene dichloride at — 35° C., and results with Iraq Raffinate show that ethylene dichloride: toluene (50/50) gives only about three-fourths as much wax as pure

TABLE III.

*Comparison of Wax Determinations with Three Solvents.*

| Oil. | Solvent. | Temperature of crystallization, ° C. | Percentage of wax found. | Remarks. |
|---|---|---|---|---|
| Iraq Raffinate | (*a*) Ethylene dichloride | — 35 | 29·9 | |
| | (*b*) Ethylene dichloride : toluene (50/50) | — 35 | 21·3 | |
| Pennsylvania Distillate | (*a*) Ethylene dichloride | — 35 | 18·9 | |
| | (*b*) Chloroform | — 55 | 17·9 | |
| Pennsylvania Bright Stock | (*a*) Ethylene dichloride : toluene (50/50) | — 35 | 1·1 | Wax from (*b*) melted about 23° C. and appeared to have less oil than that from (*a*) |
| | (*b*) Chloroform | — 55 | 1·8 | |
| Wellsville Cylinder Oil | (*a*) Ethylene dichloride : toluene (50/50) | — 35 | 9·3 | Wax from (*b*) was harder and appeared to have less oil than that from (*a*) |
| | (*b*) Chloroform | — 55 | 13·7 | |

ethylene dichloride. The determinations with Pennsylvania Bright Stock and with Wellsville (Pennsylvania) Cylinder Oil (neither miscible with ethylene dichloride) show that chloroform gives a greater amount of wax than ethylene dichloride : toluene. Since chloroform and ethylene dichloride give nearly the same result where they can both be used, it appears safe to substitute the former when the latter is not completely miscible with the oil.

2. *Fractional Crystallization of Waxes.* A comparison of data obtained with ethylene dichloride and with chloroform on a wax from Pennsylvania Distillate showed that the two solvents can be made to give almost the same results by making the final crystallization from chloroform at — 55° C., compared with — 35° C. for ethylene dichloride. Chloroform gave about 44 per cent. oil of somewhat higher than — 20° C. set-point and 56 per cent. wax, the last fraction of which melts a little below the range 18–25° C. This is fairly close to the result with ethylene dichloride, viz. 47 per cent. of oil of — 15° C. set-point and 53 per cent. wax melting above 14° C. In Fig. 3 the data are plotted as final melting point of fraction *v.* mid per cent. of fraction, and in Fig. 4 as refractive index *v.* final melting point. The final melting point is used because it is the most easily and accurately observed. Fig. 3 shows that ethylene dichloride and chloroform both

FIGURE 4 COMPARISON OF THREE SOLVENTS FOR FRACTIONAL CRYSTALLIZATION OF WAXES




FIGURE 3 COMPARISON OF THREE SOLVENTS FOR FRACTIONAL CRYSTALLIZATION OF WAXES

separate the Pennsylvania Distillate wax into nearly the same-size fractions of about the same melting point. Fig. 4 shows that although the fractions are of very nearly the same melting point, those separated by ethylene dichloride are somewhat more paraffinic than those from chloroform; the ethylene dichloride fractions, then, appear to contain less oil than the chloroform fractions.

Data obtained in fractional crystallizations from ethylene dichloride : toluene (50/50) and from chloroform of a wax from Wellsville Cylinder Oil (this oil is not miscible with ethylene dichloride alone at — 35° C.) show that although the material soluble at the lowest temperature in each case was an oil of — 10° C. set-point, 27·6 per cent. of this material was found with the mixed solvent and 36·3 per cent. with the chloroform, and that the final wax fraction separated by chloroform has the lower melting range, 10–15° C. as against 18–25° C. If the final separation from ethylene dichloride : toluene had been made at a somewhat higher temperature to give 36 per cent. oil, this oil would then be expected to have a set-point higher than — 10° C., and the last wax fraction a melting range higher than 18–25° C. Thus a clean separation of oil from low-melting wax is not possible with the mixed solvent, although it would be usable for an approximation if nothing better were available.

3. *Determination of Low-Melting Waxes.* In determinations such as those discussed under : (1) the fractions soluble at the lowest filtration temperature have been called oils, and their set-points have been reported. The last solid fraction in each was a wax with a definite melting range. It was shown that ethylene dichloride permitted sharper separation of the wax fractions than either of the other solvents. The fractional crystallization of wax from Pennsylvania Distillate from ethylene dichloride at — 35° C. gave a final fraction melting from 14° to 23° C., and a corresponding fraction from chloroform at — 68° C. melting 9–17° C. Because chloroform is not so selective a solvent as ethylene dichloride, and because at very low temperatures liquid fractions of high molecular weight may separate from it, the waxes from chloroform are probably contaminated with oil; the use of chloroform for fractional crystallization is not recommended, therefore, unless the separation of waxes of very low melting point is essential. The melting range of the last fraction from chloroform could be lowered a few degrees by crystallizing at a slightly lower temperature, but the practical limit is only a little below that used, since chloroform freezes out at about — 70° C.

## PART II.—COMPOSITION OF WAXES.

### A. Introduction.

The method described in Part I has value other than simply as an analytical method for finding the proportion of wax in oil or of oil in wax and the distribution of melting ranges in the separated waxes. The determination of the refractive indices of the fractions obtained by the fractional crystallization of a wax and their comparison with refractive indices of pure hydrocarbons affords a method for investigating the composition of the waxes present in various oils.* The information so obtained should be generally useful in the investigation of the composition of crude oils and products obtained from them, and particularly useful in relation to dewaxing problems and to the properties and compositions of lubricating oils. In addition to the determinations reported in Part I, a number of other fractional crystallizations have been made on several different waxes.

### B. Properties of Synthetic Higher Hydrocarbons.

Several recent papers have correlated the structure of pure hydrocarbons with specific refractivity, specific dispersion or solubility in one or more solvents. These properties are different for paraffins, naphthenes and aromatics, and permit a quick if somewhat approximate placing of an unknown hydrocarbon in one of these groups. Because these methods require a fairly accurate determination of the density, they are not satisfactory for samples of less than about 1 ml., unless special apparatus is available. Melting ranges and refractive indices of very small samples can, however, be determined with standard apparatus and used to classify samples. Since the wax fractions are mixtures, such a classification is as precise as is necessary. Table IV gives the properties of a number of pure hydrocarbons recorded in the literature.†

In many cases it was necessary to calculate the refractive index,‡ and in almost all cases temperature corrections were required. Since the standard temperature of 90° C. is higher than the melting point of any of the wax fractions, all recorded values are for liquids. When the melting points of the pure compounds are plotted against their refractive indices, the different series of hydrocarbons occupy different areas that overlap somewhat, as shown in Fig. 5. This overlapping is not so important as

* Fractional crystallization of waxes from ethylene dichloride is by no means new. Several papers have appeared in which its use for one purpose or another has been described, among them references 8 and 9.

† The data available are meagre, and many of them are questionable. Compounds with olefinic double bonds are not included.

‡ For hydrocarbons of about the same molecular weight and structure, the quantity $\frac{n-1}{d}$ (where $n$ is the refractive index and $d$ the density) is very nearly constant. When $\frac{n-1}{d}$ is known for a group of related compounds, the unknown refractive index of a member of the group can be got from its density.

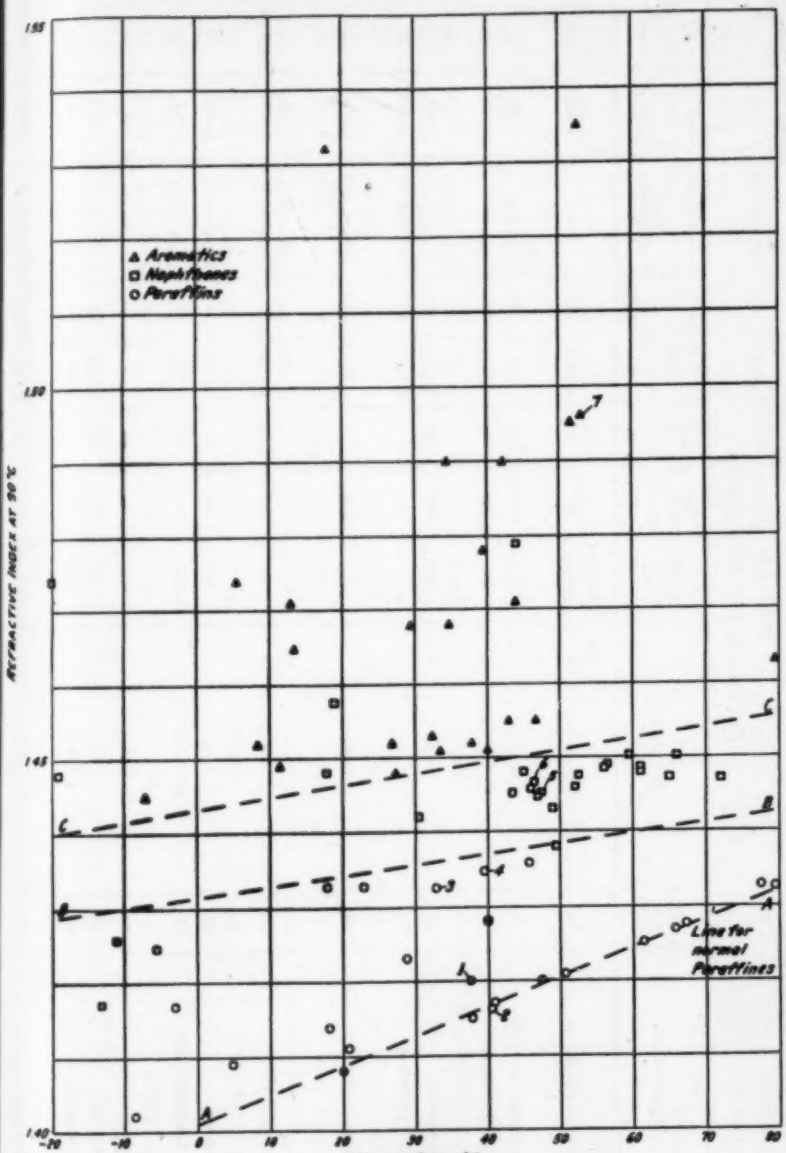
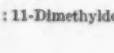
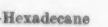
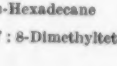
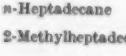
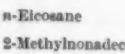
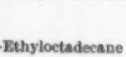
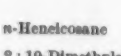
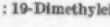
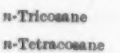
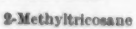
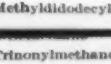


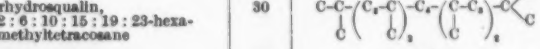

FIGURE 5 PROPERTIES OF PURE HYDROCARBONS

Order No. 7426.

TABLE IV.

*Properties of Pure Hydrocarbons.*

| Hydrocarbon. | No. of C atoms. | Structure.* | Melting point ° C. | Boiling point T° C. at p mm. | | Density $d_4^{T°}$ C. | | Refractive Index. | | Reference. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | T. | p. | d. | T° C. | From literature at T° C. | Calculated to 90° C. | |
| **A. *Paraffins.*** | | | | | | | | | | |
| 2 : 11-Dimethyldodecane | 14 |  | −8·5 | 117 | 13 | 0·7820 | 0 | — | 1·402 | 17 |
| *n*-Hexadecane | 16 |  | 20 | 287·5 | 760 | 0·775 | 20 | — | 1·408 | 12 |
| 7 : 8-Dimethyltetradecane | 16 |  | < −30 | — | — | 0·7530 | 70 | — | 1·410 | 24 |
| *n*-Heptadecane | 17 |  | 22·5 | 303 | 760 | 0·778 | 20 | — | 1·411 | 13 |
| 2-Methylheptadecane | 18 |  | 5 | — | — | 0·7469 | 70 | 1·4170 at 70 | 1·4090 | 24 |
| *n*-Eicosane | 20 |  | 38 | 205 | 15 | 0·778 | 36·7 | 1·434 at 42·9 | 1·415 | 13 |
| 2-Methylnonadecane | 20 |  | 18·3 | — | — | 0·7530 | 70 | 1·4217 at 70 | 1·4138 | 24 |
| 3-Ethyloctadecane | 20 |  | − 3 | 202 | 12 | 0·7597 | 70 | 1·4246 at 70 | 1·4167 | 18 & 24 |
| *n*-Henicosane | 21 |  | 40·4 | — | — | 0·7585 | 70 | 1·4240 at 70 | 1·4161 | 10 |
| 2 : 19-Dimethyleicosane | 22 |  | 41 | — | — | 0·7626 | 70 | — | 1·417 | 24 |
| *n*-Tricosane | 23 |  | 47·4 | — | — | — | — | — | 1·42 | 10 |
| *n*-Tetracosane | 24 |  | 50·8 | 243 | 15 | 0·7682 | 70 | 1·4288 at 70 | 1·4209 | 10 |
| 2-Methyltricosane | 24 |  | 37·7 | — | — | 0·7662 | 70 | 1·4279 at 70 | 1·4200 | 10 |
| Methyldidodecylmethane | 26 |  | 29 | — | — | 0·7720 | 70 | 1·4308 at 70 | 1·4229 | 10 |
| Trinonylmethane | 28 |  | − 5·5 | — | — | 0·7770 | 70 | 1·4325 at 70 | 1·4246 | 10 |
| | | | 65·9 | — | — | 0·7795 | 70 | 1·4348 at 70 | 1·4269 | 10 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Methyldidodecylmethane | 26 | $C_{12}$–C($C_{10}$)–$C_{10}$ | 29 | — | — | 0·7720 | 70 | 1·4308 at 70 | 1·4229 | 10 |
| Trinonylmethane | 28 | $C_9$–C($C_9$)–$C_9$ | − 5·5 | — | — | 0·7770 | 70 | 1·4325 at 70 | 1·4246 | 10 |
| n-Triacontane | 30 | $n$-$C_{30}$ | 65·9 | — | — | 0·7795 | 70 | 1·4348 at 70 | 1·4269 | 10 |
| Perhydrosqualin, 2 : 6 : 10 : 15 : 19 : 23-hexamethyltetracosane | 30 |  | −80 | — | — | 0·7784 | 70 | 1·4340 at 70 | 1·4261 | 24 |
| n-Hentriacontane | 31 | $n$-$C_{31}$ | 67·3 | — | — | 0·7827 | 70 | 1·4356 at 70 | 1·4276 | 10 |
| 6-Methylhentriacontane | 32 | $C_{12}$–C($C_{13}$)–$C_{13}$ | 32–34 | — | — | 0·7907 | 70 | 1·4401 at 70 | 1·4325 | 24 |
| 16-Ethylhentriacontane | 33 | $C_{15}$–C($C_2$)–$C_{13}$ | app. 18 | — | — | 0·7910 | 70 | 1·4404 at 70 | 1·4328 | 24 |
| 16-Butylhentriacontane | 35 | $C_{15}$–C($C_4$)–$C_{13}$ | app. 23 | — | — | 0·7913 | 70 | 1·4408 at 70 | 1·4328 | 24 |
| n-Heptatriacontane | 37 | $n$-$C_{37}$ | 77·4 | — | — | 0·768 | 100 | 1·4328 at 90 | 1·4328 | 20 |
| 18-Ethylpentatriacontane | 37 | $C_{17}$–C($C_2$)–$C_{17}$ | 39–40 | — | — | 0·773 | 100 | 1·4348 at 90 | 1·4348 | 20 |
| n-Octatriacontane | 38 | $n$-$C_{38}$ | 79·2–79·4 | — | — | 0·7688 | 100 | 1·4326 at 90 | 1·4326 | 20 |
| 18-Propylpentatriacontane | 38 | $C_{17}$–C($C_3$)–$C_{17}$ | 64–65 | — | — | 0·781 | 100 | 1·4376 at 90 | 1·4376 | 20 |
| Dipentadecylcetylmethane | 47 | $C_{15}$–C($C_{16}$)–$C_{15}$ | 45·5–46 | — | — | — | — | 1·4435 at 70 | 1·4359 | 24 |

B. *Naphthenes.*

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *cyclo*Pentane | 5 | (5 | < −80 | 50 | 760 | 0·754 | 20 | — | 1·395 | 22 & 11 |
| *cyclo*Hexane | 6 | (6 | 7 | 81·5 | 760 | 0·7387 | 80 | 1·4031 at 80 | 1·3991 | 22 & 11 |
| *cyclo*Heptane | 7 | (7 | −13 | — | — | 0·7628 | 80 | 1·4212 at 80 | 1·4171 | 22 |
| *cyclo*Octane | 8 | (8 | −11 | 144 | 730 | 0·7785 | 80 | 1·4300 at 80 | 1·4257 | 22 & 23 |
| *cyclo*Dodecane | 12 | (12 | 61 | 118 | 18 | 0·8223 | 75 | — | 1·448 | 22 |
| *cyclo*Tridecane | 13 | (13 | 18 | 112–3 | 9 | 0·8513 | 33·5 | — | 1·448 | 22 |
| *cyclo*Tetradecane | 14 | (14 | 52–53 | 143 | 16 | 0·8253 | 80 | 1·4515 at 80 | 1·4475 | 22 |

* The symbol (*n* will be used to indicate a single naphthene ring of *n* carbon atoms. Thus (6 = *cyclo*hexane.

TABLE IV (*cont.*).

| Hydrocarbon. | No. of C atoms. | Structure. | Melting point ° C. | Boiling point T° C. at p mm. | | Density $d_4^{T°}$ C. | | Refractive Index. | | Reference. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | T. | p. | d. | T° C. | From literature at T° C. | Calculated to 90° C. | |
| | | B. *Naphthenes* (contd.) | | | | | | | | |
| *cyclo*Pentadecane | 15 | (15 | 61 | — | — | 0·8227 | 80 | 1·4522 at 80 | 1·4486 | 22 |
| *cyclo*Hexadecane | 16 | (16 | 56–57 | 170–1 | 20 | 0·8190 | 79 | 1·4529 at 80 | 1·4489 | 22 |
| Methyl*cyclo*pentadecane | 16 | C–(15 | −19 | — | — | 0·8051 | 109 | 1·4438 at 102 | 1·4478 | 22 |
| Di*cyclo*octyl | 16 | 8)–(8 | < −20 | 140 | 1 | 0·9277 | 20 | 1·5018 at 20 | 1·474 | 23 |
| *cyclo*Heptadecane | 17 | (17 | 65 | — | — | 0·8187 | 80 | 1·4507 at 80 | 1·4473 | 22 |
| *cyclo*Octadecane | 18 | (18 | 72 | — | — | 0·8177 | 80 | 1·4506 at 80 | 1·4472 | 22 |
| *cyclo*Docosane | 22 | (22 | 46 | 212 | 16 | 0·8144 | 80 | 1·4481 at 80 | 1·4457 | 22 |
| *cyclo*Triacosane | 23 | (23 | 49 | — | — | 0·8259 | 64 | 1·4558 at 56 | 1·4429 | 21 |
| *cyclo*Tetracosane | 24 | (24 | 47 | — | — | — | — | — | — | 22 |
| *cyclo*Hexyloctadecane | 24 | (6–$C_{18}H_{37}$ | 40 | — | — | 0·834 | 25 | 1·4538 at 25 | 1·428 | 25 |
| *cyclo*Hexacosane | 26 | (26 | 43–44 | 218–9 | 0·5 | 0·8108 | 80 | 1·4484 at 80 | 1·4450 | 22 |
| *cyclo*Octacosane | 28 | (28 | 47–48 | 213–4 | 0·25 | 0·8103 | 80 | 1·4489 at 80 | 1·4450 | 22 |
| Octodecyldecalin | 28 | 6) (6–$C_{18}H_{37}$ | 43–47 | — | — | 0·863 | 25 | 1·4739 at 25 | 1·448 | 25 |
| 1 : 1-Di*cyclo*hexylhexadecane | 28 | $C_{16}H_{33}$–C(6)(6) | 18·5–19·5 | 269–71 | 15 | 0·8791 | 20 | 1·4862 at 17·5 | 1·4574 | 16 |
| *cyclo*Hexyldocosane | 28 | (6 –$C_{22}H_{45}$ | 49–50 | — | — | 0·8327 | 25 | 1·4643 at 25 | 1·438 | 25 |
| *cyclo*Nonacosane | 29 | (29 | 46–47 | 215 | 1·1 | 0·8232 | 64 | — | 1·4465 | 22 |
| *cyclo*Triacontane | 30 | (30 | 56 | — | — | 0·8171 | 80 | 1·4523 at 80 | 1·4485 | 22 |
| Di*cyclo*pentadecyl | 30 | 15)–(15 | 44 | — | — | 0·8728 | 88·6 | 1·4748 at 100 | 1·4788 | 23 |
| *cyclo*Dotriacontane | 32 | (32 | 59–60 | — | — | 0·8261 | 70 | 1·4568 at 70 | 1·4502 | 26 |
| 5-*cyclo*Hexylhexacosane | 32 | H (6 –C–$C_{21}H_{43}$ $C_6H_{11}$ | 30–31 | — | — | 0·8372 | 25 | 1·4677 at 25 | 1·442 | 25 |
| *cyclo*Tetratriacontane | 34 | (34 | 66 | — | — | 0·8329 | 76 | 1·4568 at 72 | ·4503 | 26 |
| | | C. *Aromatics.* | | | | | | | | |
| | | | | 5·5 | 79·6 | 760 | 0·878 | 20 | 1·5014 at 20 | 1·474 | 13 |

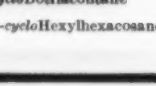
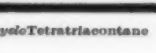
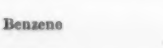
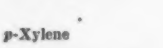
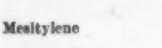
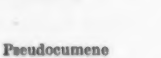
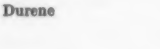
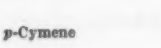
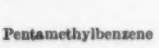
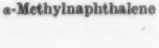
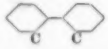
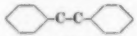
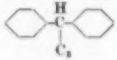
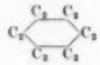
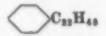
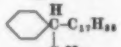
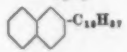
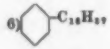
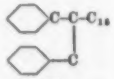
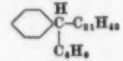
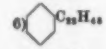
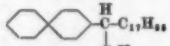
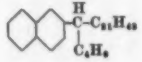
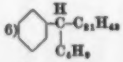
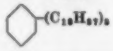
| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 5-*cyclo*Hexylhexacosane | 32 |  | 30–31 | — | — | 0·8372 | 25 | 1·4677 at 25 | 1·442 | 25 |
| *cyclo*Tetratriacontane | 34 |  | 66 | — | — | 0·8229 | 76 | 1·4568 at 72 | ·4503 | 26 |
| **C. *Aromatics.*** | | | | | | | | | | |
| Benzene | 6 |  | 5·5 | 79·6 | 760 | 0·878 | 20 | 1·5014 at 20 | 1·474 | 13 |
| *o*-Xylene | 8 | | −28 | 142–4 | 760 | 0·8802 | 20·3 | 1·5082 at 14·1 | 1·4741 | 11 |
| *m*-Xylene | 8 | | −54 to −53 | 138·8 | 760 | 0·8649 | 20·2 | 1·5008 at 15·6 | 1·4673 | 11 |
| *p*-Xylene | 8 |  | 13–14 | 138 | 760 | 0·8612 | 20 | 1·4939 at 25·4 | 1·4649 | 11 |
| Mesitylene | 9 |  | −57·5 | 162–4 | 760 | 0·8558 | 20 | 1·4912 at 20 | 1·45 | 11 |
| Pseudocumene | 9 |  | −61 | 169·3 | 760 | 0·8803 | 40 | 1·5064 at 17 | 1·473 | 11 |
| Durene | 10 |  | 79–80 | 193 | 760 | 0·8380 | 81·3 | — | 1·463 | 11 |
| *p*-Cymene | 10 |  | −73·5 | 177·3 | 760 | 0·8058 | 83·4 | 1·4966 at 7·9 | 1·458 | 11 |
| Naphthalene | 10 |  | 80·1 | 217·9 | 760 | 1·145 | 20 | 1·5827 at 99·6 | 1·5866 | 13 |
| Pentamethylbenzene | 11 | | 53 | 231 | 760 | 0·8472 | 107·2 | 1·488 at 107·2 | 1·496 | 11 |
| α-Methylnaphthalene | 11 |  | −22 | 243 | 760 | 1·025 | 20 | 1·618 at 20 | 1·590 | 13 |
| β-Methylnaphthalene | 11 |  | 35·1 | 245 | 760 | 1·029 | 20 | 1·6026 at 40 | 1·583 | 13 |
| Diphenyl | 12 |  | 69 | 254·9 | 760 | 1·041 | 20 | 1·588 at 77·1 | 1·583 | 13 |

TABLE IV (*cont.*).

| Hydrocarbon. | No. of C atoms. | Structure. | Melting point ° C. | Boiling point T° C. at p mm. | | Density $d_4^{T°}$ C. | | Refractive Index. | | Reference. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | T. | p. | d. | T° C. | From literature at T° C. | Calculated to 90° C. | |
| | | C. *Aromatics* (contd.) | | | | | | | | |
| Phenylcyclohexane | 12 | | app. 0 | 239 | 745 | 0·9441 | 20 | 1·580 at 16 | 1·560 | 11 |
| Acenaphthene | 12 | | 95 | 277·5 | 760 | 1·024 | 99·2 | 1·6048 at 98·8 | 1·6078 | 13 |
| Diphenylmethane | 13 | | 27 | 262 | 760 | 1·0064 | 20 | 1·575 at 26 | 1·550 | 13 |
| 1 : 2 : 4 : 5-Tetraethylbenzene | 14 | | 13 | 248 | 755 | 0·8884 | 16 | 1·5041 at 16 | 1·471 | 11 |
| Phenyloctane | 14 | | − 7 | 261–3 | 760 | 0·852 | 14 | — | 1·445 | 11 |
| *o* : *o*'-Ditolyl | 14 |  | 17·8 | 272 | 760 | 0·955 | 10 | — | 1·532 | 13 |
| Dibenzyl | 14 |  | 52·5 | 284 | 760 | 0·942 | 80·6 | 1·539 at 80·6 | 1·535 | 13 |
| 1 : 1-Diphenylbutane | 16 |  | 27 | 265–6 | 75 | 1·006 | 16 | 1·577 at 16 | 1·552 | 11 |
| Hexaethylbenzene | 18 |  | 129 | 298 | 760 | 0·831 | 130·4 | 1·480 at 130·4 | 1·496 | 13 |
| Phenylhexadecane | 22 | | 27 | 230 | 15 | 0·8079 | 99·2 | — | 1·452 | 11 |
| *o*-Tolylhexadecane | 23 | | 8–9 | 238·5 | 15 | 0·8072 | 99 | — | 1·452 | 11 |
| *m*-Tolylhexadecane | 23 | | 11–12 | 237 | 15 | 0·8029 | 99·3 | — | 1·449 | 11 |
| 1 : 5-Dimethyl-2-cetylbenzene | 24 | | 33·5 | 250 | 15 | 0·8062 | 99·4 | — | 1·451 | 11 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *m*-Tolylhexadecane | 23 | | 11–12 | 237 | 15 | 0·8029 | 99·3 | — | 1·440 | 11 |
| 1 : 5-Dimethyl-2-cetylbenzene | 24 | | 33·5 | 250 | 15 | 0·8062 | 99·4 | — | 1·451 | 11 |
| 1 : 3 : 5-Trimethyl-2-cetylbenzene | 25 | | app. 40 | 258 | 15 | 0·8065 | 99·2 | — | 1·451 | 11 |
| Docosylbenzene | 28 |  | 42–44 | — | — | 0·8513 | 25 | 1·4806 at 25 | 1·455 | 25 |
| 5-Phenyldocosane | 28 |  | 38 | — | — | 0·8554 | 25 | 1·4777 at 25 | 1·452 | 25 |
| Octodecylnaphthalene | 28 |  | 51–52 | — | — | 0·906 | 25 | 1·5206 at 25 | 1·495 | 25 |
| Octodecyltetralin | 28 |  | 29–30 | — | — | 0·884 | 25 | 1·4939 at 25 | 1·468 | 25 |
| 1-Phenyl-2-benzylheptadecane | 30 |  | 34·5–35 | 294–6 | 16 | 0·9165 | 20 | 1·5160 at 15·9 | 1·490 | 16 |
| 5-Phenylhexacosane | 32 |  | 32–33 | — | — | 0·8532 | 25 | 1·4787 at 25 | 1·453 | 25 |
| Docosyltetralin | 32 |  | 43–45 | — | — | 0·8786 | 25 | 1·4969 at 25 | 1·471 | 25 |
| 5-*para*-Phenylphenyldocosane | 34 |  | 41·5–43 | — | — | 0·899 | 25 | 1·5158 at 25 | 1·490 | 25 |
| 5-Naphthylhexacosane | 36 |  | 39–40 | — | — | 0·8792 | 25 | 1·5037 at 25 | 1·478 | 25 |
| *sec.*-Hexacosyltetralin | 36 |  | 35 | — | — | 0·8762 | 25 | 1·4940 at 25 | 1·468 | 25 |
| Trioctodecylbenzene | 60 |  | 46·5–47 | — | — | 0·8520 | 25 | 1·4813 at 25 | 1·455 | 25 |

might be expected, since most of the compounds in the common area, because of their boiling points, cannot be in the wax fractions. In Fig. 5 several straight lines are drawn to separate the fields. The lower limit of possible values of refractive index and melting point is the straight line (*A*) joining the normal paraffin points. The line (*B*) indicates the upper limit of the isoparaffins, and serves also as a lower limit for the naphthenes.* The line (*C*) marks the upper limit of the simple, *i.e.* single-ring, naphthenes. The data for methyl *cyclo*pentadecane and for cyclotridecane are out of line and may be inaccurate. Line (*C*) is the lower limit for the known single and condensed ring aromatics and for condensed-ring and polynaphthenes. With the exception of line (*A*), the fields are limited by bands common to both fields, the width of which may be expected to increase as more of the higher hydrocarbons become known.

The melting point : refractive index relation of pure hydrocarbons only has been considered above, but a wax fraction, even after careful fractional crystallization, contains a number of chemical individuals. The refractive index of such a fraction will be a weighted mean of the refractive indices of the components, but its melting point (or range) may be lower than the mean, owing to deviations from Raoult's law. The little information available indicates that mixtures of paraffins and aromatics or of different aromatics may form eutectic mixtures, but that mixtures of closely related paraffins form solid solutions.[7] The result of these effects will be that if the properties of a wax mixture, plotted in Fig. 5, fell on point 1, for example, giving the properties of 2-methyltricosene, an *iso*-paraffin ($n_D^{20}$ 1·42, melting point 37·7° C.), the mixture might still consist chiefly of the normal paraffin heneicosane, point 2, with smaller amounts of *iso*paraffins such as those represented by the points 3 and 4, with even smaller amounts of naphthenes such as are represented by the points 5 and 6, or with traces of higher aromatics such as pentamethylbenzene, point 7. To sum up, then, the observed melting point of a fraction may be the mean of the melting points of the components, or may be below the melting point of either owing to eutectic formation.

### C. Hydrocarbon Types Present in Distillate Waxes.

In Fig. 6 the melting point *v.* refractive index curves of the fractions of a number of distillate waxes are plotted.† Curves of this type will be called "characterizing curves," since they permit certain conclusions about the character of the wax fraction. The fields of the three hydrocarbon types, defined above, are indicated in the figure. All these curves are of similar shape; each consists of two parts joining in a region of minimum refractive index. The portion of each curve in the region of higher melting points lies nearly parallel, and fairly close to the line for normal paraffins. As the curve progresses into the region of lower melting points, it rises rapidly above the normal paraffin line, crossing the *iso*paraffin and simple

* Naphthenes (*cyclo*alkanes) of less than eight carbon atoms lie below this line, but their boiling points are so low that they cannot be present in the waxes.

† Since the region of higher melting points is the one of greatest interest in Figs. 6, 7 and 8, the scale of these figures is double that used in Fig. 4, and a few points in the aromatic region are not shown.

naphthene fields into the aromatic and polynaphthene field. Thus the higher-melting fractions of distillate waxes are chiefly normal paraffins, whereas the lower-melting fractions are rich in naphthenes or aromatics.

The minima in the characterizing curves for distillate waxes may be explained as follows. The shape of the curves is dependent on the relation of the properties of the members of the several hydrocarbon series present in the wax. Of the hydrocarbons boiling within any given range, the melting points will usually increase in the order aromatics, naphthenes, *n*-paraffins, but the refractive indices will decrease in that order. Fractional crystallization separates mixtures into groups the constituent hydrocarbons of which have about the same melting point, and mixtures of the three hydrocarbon types of very narrow boiling range should give three sections of curve, each sloping down to the left, one in each field, from the region of paraffins with high melting points and low refractive indices, through the region of naphthenes with intermediate melting points and refractive indices, to the region of low-melting-point, high-refractive-index aromatics. As the boiling range of the cut from which the wax is taken increases, the discontinuities in these sections will become less clear owing to overlap; and in the extreme case even the high-melting fractions will contain large proportions of high-boiling naphthenes. Distillate cuts, which have narrow boiling ranges compared to residues, should therefore show the type of characterizing curve found.

It follows that consecutive distillate cuts should contain consecutive members of each hydrocarbon series. The characterizing curves for waxes from two such cuts—a gas oil obtained in the preparation of a Ventura (California) Distillate and the distillate itself, given in Fig. 6—indicate that this is so; the evidence is clearest for the *n*-paraffins, the curves for which are nearly continuous. This circumstance suggests that all the *n*-paraffins boiling within the range of the two distillates are present in the waxes from them. In the region of the *iso*paraffins, naphthenes and aromatics, the presence of a large number of compounds is possible, and each fraction may be expected to contain members of more than one series.

Coalinga oil is known to be very aromatic, but a distillate wax from this oil (Fig. 6) was found to contain large amounts of paraffins in the higher-melting fractions, an important fact because it shows that the high-melting fractions of even the most aromatic oils are rich in paraffins.

Commercial paraffin wax (Parowax) from the Standard Oil Company of New Jersey had an A.S.T.M. melting point of 51·5° C. Its melting range was 46–55° C. under the microscope. It was separated by fractional crystallization from ethylene dichloride into fractions melting over the rather short range 37–64° C. As the curve in Fig. 6 shows, it consists almost entirely of normal paraffins.

The curves of melting-point distributions for those waxes, similar to those shown in Fig. 3, give little useful information about the waxes and are therefore omitted.

### D. Hydrocarbon Types in Residue Waxes.

A residual oil has an initial boiling point near the final boiling point of the last distillate taken off, but the boiling point of the heaviest hydro-

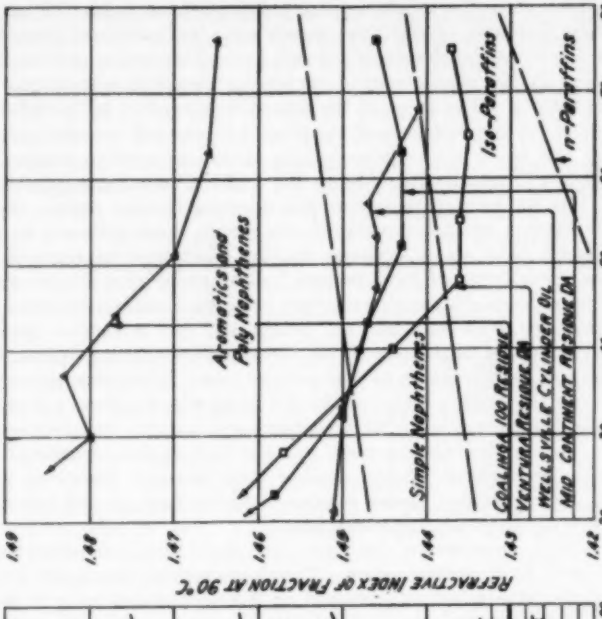



FIGURE 7 CHARACTERIZING CURVES OF RESIDUE WAXES

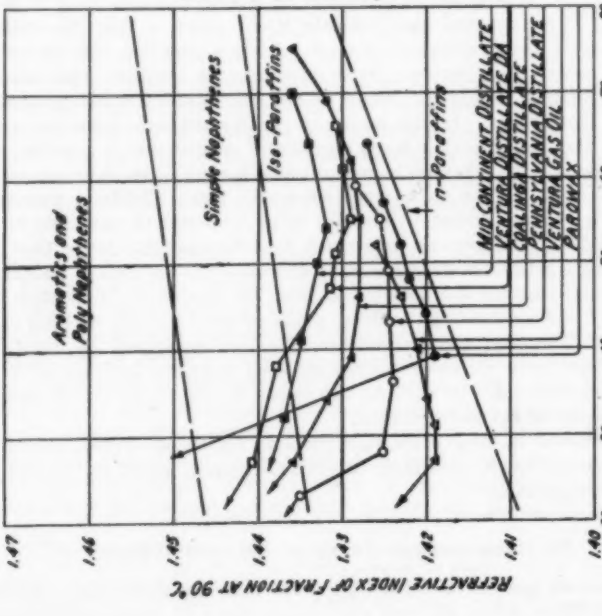



FIGURE 6 CHARACTERIZING CURVES OF DISTILLATE WAXES

carbon is not attainable. An oil of such a wide boiling range must contain many more members of each hydrocarbon series than a distillate cut. The characterizing curves of three residue waxes are shown in Fig. 7. The portion of minimum refractive index has disappeared * in two of them, and even the highest-melting fractions are not very near the *n*-paraffin lines. This does not mean that *n*-paraffins are absent, but rather that large amounts of non-paraffins are present. Although it is not necessary to assume that normal paraffins are absent to explain the position of the curve, there are two ways in which the higher normal paraffins could have been removed from the oil. Firstly, they may have separated in the ground before reaching the well, or in the well itself as, for instance, *rod waxes*.[9] Secondly, the higher paraffins are more sensitive to thermal decomposition than the lower ones, and may have cracked in the topping of the crude.

It is interesting to note that though Ventura Residue is considered a more aromatic oil than Mid-Continent Residue or Wellsville Cylinder Oil, the wax from it is less aromatic than those from the other two oils.

### E. Hydrocarbon Types in Petrolatum.

An amber petrolatum and a white petrolatum have been subjected to analytical crystallization. The difficulty in filtration that might have

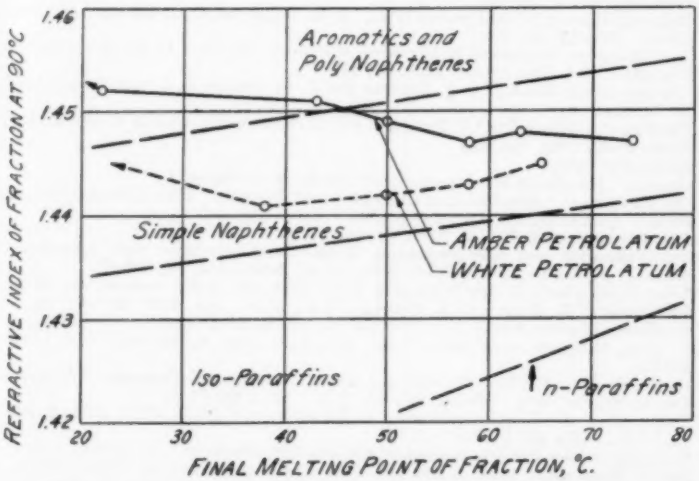



FIGURE 8. CHARACTERIZING CURVES OF TWO PETROLATUMS

been anticipated from the supposed micro-crystalline structure of these materials did not appear, all the fractions filtering as easily as the wax

* The Mid-Continent Residue DA lost some high-melting non-paraffins in being deasphaltized. The effect was to increase slightly the concentration of paraffins in the high-melting wax fractions and to cause the minimum in the curve for this material.



FIGURE 7 CHARACTERIZING CURVES OF RESIDUE WAXES

FIGURE 6 CHARACTERIZING CURVES OF DISTILLATE WAXES

fractions from distillates. As is shown in Fig. 8, the higher-melting fractions seem to be naphthenes, and though a careful refractionation of them might yield some paraffins, they are less paraffinic than most of the distillate waxes studied. The amber product contained 63 per cent. of an oil of — 20° to — 25° C. set-point, the white, 43 per cent. of an oil of — 30 to — 35° C. set-point. Obviously the samples were not soft waxes, but mixtures of moderately hard waxes and oils of low pour-point. The evidence points to residues as the sources of the petrolatums. The white material was somewhat less aromatic than the amber product, the differences being similar to those that have been obtained by the acid treatment of waxes.

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# CORRESPONDENCE.

*To the Editor.*

Dear Sir,—In his interesting article about the aniline points of hydrocarbons * Dr. E. B. Evans says: " . . . It may be remarked that no compound containing an aromatic nucleus has been examined the aniline point of which is not well below 0·0° C., and, in consequence, no data are given for this class of compound." I take the opportunity to say, that some time ago K. S. Kurindin and I † have determined the critical solution temperatures (C.S.T.) in aniline for several aromatic hydrocarbons, synthesized by us. The C.S.T.'s of these hydrocarbons, together with some other constants, are given below. I have also included the C.S.T. in aniline of dotriacontane, described in another place,‡ which may present some interest.

*Critical Solution Temperature in Aniline of some Hydrocarbons.*

| No. | Hydrocarbon. | Empirical Formula. | Boiling Point, ° C. | Pressure, mm. | Melting Point, ° C. | Specific Gravity. | | | C.S.T. in Aniline, ° C. | $n_D^t$ | $t$° C. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $d_4^{t_1}$ | $d_4^{t_2}$ | $t$° C. | | | |
| 1 | Octylbenzene (2-phenyloctane) | $C_{14}H_{22}$ | 115·5–118·5 | 6 | — | 0·878 | 0·859 | 20·5 | < −17 | 1·4861 | 18·4 |
| 2 | Nonylbenzene (2-phenylnonane) | $C_{15}H_{24}$ | 143–147 | 12 | — | 0·877 | 0·860 | 22 | −10·1 | 1·4869 | 21·5 |
| 3 | Decylbenzene (2-phenyldecane) | $C_{16}H_{26}$ | 131–133 | 3 | — | 0·877 | 0·862 | 19 | − 0·6 | 1·4856 | 22 |
| 4 | Undecylbenzene (2-phenylundecane) | $C_{17}H_{28}$ | 142–146 | 6 | — | 0·875 | 0·857 | 23·5 | + 8·1 | 1·4829 | 18·7 |
| 5 | Hexadecylbenzene (2-phenylhexadecane) | $C_{22}H_{38}$ | 191–194 | 6 | — | 0·880 | 0·864 | 20 | +41·1 | 1·4839 | 18·8 |
| 6 | Dotriacontane (dicetyl) | $C_{32}H_{66}$ | — | — | 71 | — | 0·775 | 80 | 127·6 | 1·4323 | 71 |

M. D. TILITSHEYEV.

*Ul. Gorkovo (Tverskaya) 50. kv. 38.*
*Moscow, 104.*
May 25th, 1937.

*To the Editor.*

*Estimating Bituminous Content of Limestone.*

Dear Sir,—In your last issue for July, No. 165, there is a contribution from Mr. L. J. Chalk referring to my short paper on the above subject.

Mr. Chalk's contention seems to be that the additional bituminous content found by the method put forward by myself should not be classified as soluble bitumen, as it was not extracted by the standard solvent, Carbon Bisulphide.

* E. B. Evans, *J.I.P.T.*, 1937, **23**, 222–225.
† M. D. Tilitsheyev and K. S. Kurindin, *Nephtianoie Khosiaistvo*, 1930, 586–598.
‡ M. D. Tilitsheyev and A. L. Feighin, *Transactions of the Conference on Cracking and Hydrogenation*, Moscow, 1931, 272.

The British Standards Institution define soluble bitumen as those hydrocarbons which are soluble in carbon bisulphide.

Mr. Chalk seems to have missed the point definitely stated in my paper that all the bitumen extracted by my method was readily soluble in carbon bisulphide, after extraction, although it did not seem possible to use this solvent for complete extraction.

Further, I consider that my total bitumen differed from the case cited by Mr. Chalk, where he used ether and hydrochloric acid to decompose the lime soaps contained in his sample of Egyptian bituminous rock and to dissolve the bituminous acid set free from these soaps, as I do not think the solvent used by myself, trichlorethylene, can have decomposed the bituminous soaps and set free the acids. I would call attention to the last sentence of the second paragraph of Mr. Chalk's communication which reads as follows :—

> "The position is naturally altered if the bitumen is actually soluble in carbon disulphide, but is adsorbed in such a manner that it cannot be extracted with the cold solvent under normal conditions. In this case it would certainly appear that some modification of the standard method is desirable."

I venture to suggest that my experiment gives an actual example of such altered position.

I am,
Yours faithfully,
ARTHUR A. ASHWORTH.

18, *St. Swithin's Lane,*
*London, E.C.* 4.
August 3rd, 1937.

*To the Editor.*

*Estimating Bituminous Content of Limestone.*

Dear Sir,—In reply to Mr. Ashworth, the purpose of my earlier letter was to suggest a possible alternative explanation for his anomalous results for the soluble bitumen content of a rock asphalt. It is to be regretted that Mr. Ashworth in his reply has not given the source of the rock asphalt with which he experimented, as this information, in conjunction with data we have on many different commercial rock asphalts, would have been most valuable, especially as regards asphaltous acid content and the behaviour of the inherent "bitumen" to different solvents.

I indicated in my previous letter that differences between the cold carbon disulphide and hot trichlorethylene extracts would be anticipated, if

(1) The rock asphalt contained a considerable proportion of asphaltous acids in the form of soaps, as in the case of the Egyptian rock asphalt I quoted.
(2) Precautions were not taken to remove free acid from the trichlorethylene and prevent its formation by hydrolysis during the hot extraction process.

The leakage of water into the hot extraction apparatus mentioned by Mr. Ashworth in the latter part of his paper may have a material bearing on the second point.

The fact that the bitumen extracted with hot trichlorethylene was soluble in cold carbon disulphide was not missed by me, as this would naturally be the case in the above circumstances. Further, the paragraph of my letter which Mr. Ashworth quotes clearly applies only if his adsorption theory is the correct explanation of the facts, which at present is open to doubt.

I am,
Yours faithfully,
L. J. CHALK
(*Chief Chemist*).

*Geochemical Laboratories*,
92, *Victoria Street*,
*Westminster*, *S.W.* 1.
August 10th, 1937.

GUSTAV EGLOFF, PH.D., M.A.

[*To face p.* 645.

UNIV. OF MICH.

# SYNTHETIC PRODUCTS FROM PETROLEUM.*

By Gustav Egloff, Ph.D., M.A. (Member).

## 1. Introduction.

The first president and founder member of our Society, Sir Boverton Redwood—whose work goes back over fifty years—took out a patent for cracking oils in the year 1891 with Sir James Dewar, an outstanding physicist. Little did they recognize what effects the cracking of oil would have on modern civilization by producing gasoline, lubricants for automobiles and aeroplanes, and many other products unknown at that time.

It is recorded that in the U.S.A. cracking was discovered accidentally by an operator in 1861 who let his still run while away, and, instead of obtaining a heavy distillate oil, made kerosene. However, Atwood obtained a U.S. patent in 1859 for the cracking of oils.

It is a far cry from the early days of shell still-cracking to produce kerosene (for then gasoline was an unwanted product) to the modern production of gasoline. When Dr. William M. Burton came out with the first commercial operation in 1913 with an 8-ft. diameter still, 30 ft. long, to produce gasoline by cracking gas oil, the capacity of this pressure still was only 125 barrels a day, producing a 30 per cent. yield of gasoline. Now, topping, cracking and polymerizing units will treat more than 35,000 barrels per day of crude oil with yields of over 70 per cent. of 70-octane gasoline.

Dunstan, Lomax and Thole were the first to collate the literature of cracking to 1915, and a beautiful job they made of it. The references that were given were many, but the art of cracking has developed to such a degree that the number of references for a single year 1936 is greater than all the work carried out prior to the year 1915.

Our President, Colonel Auld, in the year 1935 stated in a review of the past twenty-five years of petroleum that "cracking was the balance wheel of the oil industry," and I believe he is wholly right. Every branch of science and human knowledge is called upon by the oil industry to locate new oil-fields, obtain more oil from old fields, increase the value of products and to synthesize new substances from crude oil, thereby founding new industries.

Not only has the modern cracking process produced 303,452,000 barrels of motor fuel in the refineries of the world (during 1936 from 786,000,000 barrels of heavy oils) but it has also developed a host of new products such as polymer and *iso*-octane gasolines, lubricating oils, drying oils, resins, ethers, alcohols, glycols, chlorinated compounds, alkylated paraffins, aromatics and phenols. One of the effects of cracking is its mighty oil conservation force. In the year 1936 the volume of oil conserved in the world due to the cracking process was 1,865,000,000 barrels of crude. To

* First Branch Lecture delivered before a meeting of the Institution in London on 8th June, 1937; subsequently delivered before meetings of the South Wales and Northern Branches on 9th and 11th June, respectively.

produce 1,742,000,000 barrels of gasoline would have required 3,607,000,000 barrels of crude, representing a conservation of 1,865,000,000 barrels of crude in a single year.

The modern trend in the oil industry is towards catalytic reactions of hydrocarbons, in order to control the quality of product desired, instead of taking what nature has produced through the æons of time in the earth's crust. There are hundreds of different hydrocarbons in our gasolines and lubricants which cannot do a precise piece of work. Modern researches are directed towards synthesizing single definite structured hydrocarbons for specific uses. It may well be that single hydrocarbons will be devoted to use as motor fuels, lubricants and other needs of our modern civilization.

From the chemical point of view, it is absurd to put into an engine with air gasoline as nature produced it or that produced by the cracking process. A fuel charge passes into the cylinders with air, and several hundred different hydrocarbons, each one of which is competing for the oxygen with widely different velocities of oxidation, and all we get is an average overall result.

The chemist is changing that type of picture. It can readily be predicted that the motor fuels of the future will have but few, if not single hydrocarbons suitable for motor use which will more than double the efficiency of to-day. We are producing commercially, practically pure *iso*-octane from cracked gases by catalytic selective polymerization. The volatility of *iso*-octane makes it unsuitable for aeroplane use as such at this time. However, *iso*pentane having an octane rating of 91 is available in enormous volumes, and can be blended with the *iso*-octane. A 50/50 mixture would give a 94 octane rating, and tetra-ethyl lead could be added to the mixture to produce a fuel having an octane rating of over 100 if desired. But there are no motors available at the moment that can utilize efficiently that quality of fuel. However, they will be developed.

## 2. Polymerization.

### (A) *Gasoline.*

The commercial value of hydrocarbon gases from the cracking process has been greatly enhanced by the growing demand for high-octane motor fuels. Through this polymerization development the world refining industry has made potentially available an annual production of 300,000,000 barrels of motor fuel [1] having an octane rating ranging from 76 to 100. The hydrocarbons present in the motor fuels range from olefins, branched-chain paraffins such as *iso*-octane, to aromatics, depending on the process used.

The three polymerization processes in commercial operation or projected have a yearly production of over 11,315,000 barrels of 76 to 100 octane gasoline (1st August, 1937). Two of the processes are thermal and one is catalytic.

The "unitary thermal process" [2] (Polymerization Process Corp.) treats olefinic or paraffinic gases, producing therefrom gasoline and gas oil. The operating conditions range in temperature from 950 to 1100° F. and pressures of 1000 to 3000 lb. per square inch. The optimum conditions to produce the end-product desired depend on and vary with the composition of the hydrocarbon gases processed. The octane rating of the motor fuel

is about 76, with blending values of from 83 to 92 when mixed in 50 per cent. concentration in reference fuel "A."

The "multiple coil polymerization"[3] (Pure Oil Company) produces motor fuel from paraffin and olefin gases at temperatures ranging from 900° to 1000° F. and pressures of 600 to 800 lb. per square inch, termed the "primary" polymerization operation of "high pressure–low temperature." The paraffin gases from this operation are then subjected to a cracking temperature of over 1300° F., which is a preparatory step to the polymerization reaction carried out at 1150° to 1300° F. and pressures of 50 to 75 lb. per square inch. Under these operating conditions the products are gasoline, fuel oil and tar. At the lower temperatures of operation, the octane rating of the motor fuel is between 78 and 80 and on a blending basis the octane rating is 96. However, when operating the "multiple coil unit" at the highest temperature given, the octane blending value of the gasoline ranges between 105 and 135. The yield of liquid product is given as 4·4 gallons for a typical run or 3·7 *gallons of gasoline* per thousand cubic feet of gas subjected to the operating conditions.

The catalytic polymerization process[4] (Universal Oil Products Company) operates on cracked gases and on dehydrogenated propane and butanes. The liquid produced boils entirely within the gasoline range, and has an octane rating from 80 to 85, or upon a blending basis 90 to 135, depending on the quality of gasoline with which it is blended. The method of operation of this process consists of reacting the olefinic gases at a temperature of 450° F. and pressures around 200 lb. per square inch in the presence of a solid phosphoric acid catalyst. Catalytic dehydrogenation of paraffinic gases takes place at 950° F. and atmospheric pressure followed by catalytic polymerization. The yield of motor fuel per thousand cubic feet varies as a function of the olefin percentage in the gas and the source of the gases from the cracking unit. On the basis of the gas containing 36 per cent. of propene and butenes, the yield of motor fuel (10 lb. Reid vapour pressure) is 8·3 gallons per 1000 cubic feet. On the basis of catalytically dehydrogenating the propane–butanes from the residue gas from the polymerization unit, the yield is increased another 3·8 gallons or a total of 12·1 gallons gasoline per thousand cubic feet of starting gas.

One catalytic polymerization unit will process about 27 million cubic feet of cracked gas per day. This unit will produce roughly 110,000 gallons of 81 octane rating gasoline. Another plant of 15 million cubic feet capacity will produce on the order of 60,000 gallons per day, and the sizes run down to as low as 4,000 to 5,000 gallons of gasoline per day.

The susceptibility of polymer gasoline to tetraethyl lead—meaning thereby the increase of octane rating as a function of the addition of tetraethyl lead—is poor. Its susceptibility to antioxidants is high, having an induction period of about 30 minutes, which can be increased with 0·001 per cent. of antioxidant to an oxygen stability of 300 to 400 minutes. This permits storage of the gasoline when desirable for a year or longer.

### (B) Iso-*Octane*.

The manufacture of *iso*-octane having 100 octane rating in large quantities has had a profound influence on the design and operation of modern motors.

The chemist has been able to develop, from theoretical structures and from experimentation, the fact that the branch-chain paraffin hydrocarbons or the compacted ones burn slowly in an automotive engine. From the former laborious method of producing *iso*butenes from butyl alcohol, and synthesizing *iso*-octane, we are able to polymerize the normal and *iso*butenes present in the butane and butene fraction derived from the cracking process. The butenes react with one another and then, on hydrogenation, are converted into 90 to 100 octane motor fuel.

The manufacture of *iso*-octane catalytically is in operation or projected at the rate of 2,500,000 barrels a year (1st August, 1937).

By the use of 100 octane motor fuel it has been estimated by D. P. Barnard that each pay load could be increased by $2000 on the China Clipper ships flying from California to the Orient. In engines designed to make use of the higher-quality fuels, it has been estimated that each additional octane number is worth from two to five cents per gallon in the earning power of the gasoline. A limiting factor on the value of octane increase is that the heat value must be maintained, or the octane increase must be discounted by about two numbers for each per cent. lowering in heat content of the fuel compared to hydrocarbons, if fuels such as ethyl alcohol, ethers or ketones are used. Hydrocarbon fuels contain the highest energy content on a weight basis, and therefore higher octane ratings mean increased take-off and pay-load ability and cruising range.

### (C) *Lubricating Oils.*

Polymerization of olefins for the manufacture of lubricating oils has been carried out using aluminum chloride as a catalyst. Mixtures of hydrocarbons such as those found in highly cracked gasoline or single hydrocarbons such as propene, butenes or pentenes may be converted into lubricants.

The aluminum chloride polymerization of olefins yields high-boiling lubricants. Lubricating oils were produced by thermal polymerization of ethylene,[5] completing the polymerization by treatment with aluminum chloride at room temperature. From the thermal reactions of the gaseous olefins it appears that the more straight chain the molecule is, the less readily it will polymerize. It would be expected that these relationships hold even when aluminiun chloride is present, and this appears to be borne out by the report that aluminum chloride polymerizes ethylene, propene, 1-butene, 2-butene, *iso*butene, 1-pentene, 2-pentene, 2-methyl-1-butene, 3-methyl-1-butene, trimethylethylene, 1-hexene, 1-octene and cetene primarily into high-boiling liquids.[7] The results of the experiments show that the more branched the olefin structure, the poorer the lubricating quality of the oil becomes, owing to the high change in viscosity as a function of temperature rise. The long-chain paraffin hydrocarbons are reported superior lubricants compared to the *cyclo*paraffins, olefins and aromatics. Since the viscosity factor of the oil is important, the paraffins produced should be large molecules. Starting with the lower olefins, polymerization should proceed slowly in order that long-chain molecules be built up; and it was found that the amount of paraffinic oil depended on the contact time.[8]

Aluminum chloride weakens the bonds in the olefins, and if the hydrocarbons are treated to build higher paraffins, the action of the catalyst should not be so vigorous that the hydrocarbon molecule will split into small radicals. Therefore a low concentration is desirable, as shown by the use of 3 to 5 per cent. aluminum chloride in the polymerization of olefins to lubricating oils.

Characteristics of a very highly polymerized oil useful as blending in other lubricants to increase their viscosity and wear properties is present in the polymer product called paratone, the properties of which are shown in Table I.

TABLE I.

| | |
|---|---|
| Gravity °A.P.I. | 28·3 |
| Viscosity (U.S.S. @ 100° F.) | 55,600 |
| Viscosity (U.S.S. @ 210° F.) | 3,180 |
| Viscosity Index | 130 |
| Flash Point, Open Cup, °F. | 436 |
| Pour Point, °F. | +30 |
| Conradson Carbon, % | 0·04 |
| Colour, Tag Robinson | 10·75 |

This oil gives highly increased wearing qualities when added in small percentages to certain lubricating oils derived from crude oil. The estimated increase in the life of a lube oil of 100 viscosity index from Pennsylvania crude to which this highly polymerized oil has been added, has been of the order of 40 per cent.

### (D) *Resins.*

As the polymerization of olefins and diolefins increases, the molecular weight of the products formed increases, with properties varying according to the severity of the reaction conditions and the catalyst used. High-molecular-weight polymers range from viscous oils to crepe, rubber-like materials and hard resins. *iso*Butene is used as the foundation material for many of these reactions. The polymers are marketed as Vistanex products, having molecular weights ranging from 10,000 to 80,000. A solid, crepe, rubber-like material is used as an acid- and alkali-resisting material, and also to prevent weathering and ageing. As a coating it may be used on tanks, textiles, paper and rubber articles. In different modifications it may be used as a plasticizer and stabilizing agent for Neoprene, Thiokol, chlorinated and sulphated rubbers, paraffins, and halogenated compounds. Waterproofing agents, adhesives, asphalts, pitches and resins are also compounded with Vistanex, which gives them certain qualities they do not otherwise possess.

Resins from highly cracked petroleum distillates[9] are produced by the action of aluminum, iron or zinc chlorides as catalysts. Other chlorides known to have the same effect are antimony, indium, titanium and tin, as well as such organic compounds as benzene sulphonic acid, propyl alcohol saturated with hydrogen chloride, ethyl sulphate and aniline hydrobromide. Due to the quick-drying properties of these resins, they are finding extensive application either alone or in combination with the glyceride oils such as linseed. The drying time of these oils is equal to that of the most expensive lacquers, particularly if resinates and linoleates of cobalt and manganese are added to the varnishes.

The resin industry has found many uses for the cracked products from petroleum, and the economics involved in the natural rubber and resin industry are recognizing that fact, by making use of the synthetic product to improve the natural material.

A reasonably large business has been built up in the States on drying oils which are substitutes for linseed, Perilla, chinawood and that type of quick-drying oils. The manufacture of these oils is by the polymerization of highly cracked gasoline with a relatively high percentage of diolefins with fullers' earth, which produces a product highly competitive with linseed oil, and which in many cases is far superior. The refiner was obtaining about 25 cents a gallon for this drying oil at the time gasoline was selling for 4 cents a gallon at the refinery.

### 3. Dehydrogenation.

The olefin hydrocarbons are extremely valuable as source material for polymerization to gasoline, lubricating oils, drying oils, resins, rubber and many chemical derivatives. In addition to cracked products, there is a vast potential source of olefins from the paraffin hydrocarbons in petroleum and natural gas. The yearly production in different parts of the world of natural and refinery gases is over 3000 billion cubic feet. These gases contain methane, ethane, propane, butanes, etc.

A large amount of research work has been carried out along dehydrogenation lines using various temperatures with and without catalysts.

In the thermalizing of ethane, Fischer–Pichler [10] at temperatures of 1050° C. and 0·1 atmosphere obtained a yield of 74 per cent. of ethylene and 8 per cent. of acetylene based upon the *ethane reacting*. When the temperature was raised to 1350° C. a yield of 86 per cent. of acetylene and 2 per cent. of ethylene resulted. Hague and Wheeler [11] found that 90 per cent. of ethane actually decomposed and was converted into ethylene at a temperature of 700° C.

Another index of the oil-industry is acetylene-making. There is a large-scale plant which is in operation producing high yields of acetylene by means of the electric arc from hydrocarbon gases. How soon we shall be able to produce acetylene in a large way competitive with calcium carbide is not clear, but it is reasonably certain that it will be worked out by a catalytic process. The catalytic dehydrogenation of ethane to ethylene to acetylene has been accomplished on a small scale.

When thermally treating propane, Hague and Wheeler found that the

Table II.

| Products. | Mols Produced per 100 Mols of Propane Reacting | |
|---|---|---|
| | At 650° C. | At 725° C. |
| $CH_4$ and $C_2H_4$ . . . . . | About 38 | About 48 |
| $C_2H_6$ and $H_2$ . . . . . | „ 51 | „ 42 |
| $C_2H_6$ . . . . . | „ 10 | „ 8 |
| $C_4H_{10}$ . . . . . | „ 5·5 | „ 5 |

reaction of dehydrogenation to propene was 35 to 39 per cent. while 60 per cent. of the propane decomposed to methane and ethylene at 700° C.

The temperatures necessary for thermal dehydrogenation also promote decomposition and secondary reactions. Schneider and Frolich [12] found the products from a primary decomposition of propane, shown in Table II.

When reactions of propane were studied by Tropsch, Thomas and Egloff [13] at temperatures of 555° and 585° and 50 kilograms per sq. cm. pressure, in stainless steel (18–8 chrom-nickel), they concluded that the following reactions were taking place in the amount indicated :

$C_3H_8 \longrightarrow C_3H_6 + H_2$ . . . . . 6·8 per cent.
$C_3H_8 \longrightarrow C_2H_4 + H_4$ . . . . . 22·0 „
$2C_3H_8 \longrightarrow C_3H_6 + C_2H_6 + CH_4$ . . . . 54·0 „

At a later time, Egloff, Thomas and Linn [14] found that a maximum concentration of propene of 14·5 per cent. appeared in the exit gas when temperatures of 700° C., atmospheric pressure and 7 seconds contact time were used.

In the thermal reactions of butane the primary products formed are methane, ethane, ethylene, propene and butene. In Table III of Neuhaus and Marek [15] the extent of formation of each of these compounds at 600° and 650° C. is shown.

TABLE III.

*Primary Decomposition of* n-*Butane.*

| Products. | Mols of Each Product Formed Per 100 Mols of *n*-Butane Reacting | |
|---|---|---|
| | At 600° C. | At 650° C. |
| $CH_4$ and $C_2H_6$ . . . | 48·5 | 48 |
| $C_2H_6$ and $C_3H_4$ . . . | 34·5 | 37·7 |
| $H_2$ and $C_4H_8$ . . . | 16·0 | 12·3 |

At these temperatures no butadiene nor higher hydrocarbons were formed.

When Tropsch and Egloff [16] treated *n*-butane at 1100° C., at pressures of 50 mm., they found 25·8 per cent. acetylene, 92·3 per cent. ethylene and 22·2 per cent. propene. Hydrogen and paraffin were also formed, but no butane.

Frolich and Wiezevich [17] obtained 8·1 per cent. butene at 670° C. They found the temperature ranges shown in Table IV for maximum yields of given products from *n*-butane.

TABLE IV.

| Product. | Temp., ° C. | Per cent. |
|---|---|---|
| Ethylene . . . . . | 730 | 29 |
| Propene . . . . . | 650 | 11·1 |
| Butene . . . . . | 670 | 8·1 |
| Maximum total unsaturates . . | 690 Approx. | 42 |

According to Sullivan, Ruthruff and Kuentzel,[18] *n*-butane may decompose according to the following reactions:

$$C_4H_{10} \longrightarrow C_4H_8 + H_2$$
$$C_4H_{10} \longrightarrow C_3H_6 + CH_4$$
$$C_4H_{10} \longrightarrow C_2H_4 + C_2H_6$$
$$C_4H_{10} \longrightarrow C_2H_4 + C_2H_6 \longrightarrow 2C_2H_4 + H_2$$

In the thermal method of producing olefin hydrocarbons from paraffins, there are other substantial reactions taking place, such as de-methanation and de-ethanation from propane and butanes. However, when catalysts[19] are used, the reaction takes place to over 95 per cent. of the olefin desired, such as ethylene, propene and butenes from the corresponding paraffins. The temperature of ethylene and hydrogen formation from ethane catalytically is 600° C., propene from propane at 550° C. and for butenes from butanes 500° C. and atmospheric pressure. The catalytic dehydrogenation of these hydrocarbons suppressed the de-methanation and de-ethanation reactions, which are such dominating ones in the purely thermal treatment.

The catalytic dehydrogenation of paraffins can be so controlled that about 50 per cent. of olefins are produced, so that we have mixtures of paraffins and olefins which lend themselves nicely to the alkalytion reaction.

### 4. Alkylation of Paraffins.

One important direction of research in hydrocarbon chemistry was the discovery of Ipatieff and Grosse[20] that an olefin would react with a paraffin. This opened a new road to construct branch-chained paraffins from cracked gases which contain olefins and paraffins. This process of producing branch-chained paraffins is important, due to their high anti-knock value in present day automotive engines.

Alkylation of paraffins takes place at ordinary temperatures and 5–20 atmospheres pressure in the presence of a catalyst consisting of boron fluoride, nickel and water. Other catalysts used for alkylation reactions are the metallic halides of aluminum, boron, beryllium, titanium, zirconium, hafnium, thallium, columbium and tantalum.

The alkylation of *iso*butane with ethylene was carried out in the presence of boron fluoride, finely divided nickel, and water at 25° C. The reaction went nearly to completion. Factors influencing the reaction and products are: (1) Increased ratio of boron fluoride to available paraffin increases the rate of alkylation; (2) The nature of the product is dependent on the number of ethylene molecules reacting with *iso*butane. The gasoline content of the liquids produced ranged from 37 to 97 per cent., depending on the conditions of the experiment. Paraffins alone are formed, and the reaction is decidedly different from that of polymerization of ethylene, where autodestructive alkylation occurs as well as other side reactions.

The compounds formed are shown with their volume per cent. of yield in Table V.

Alkylation of *iso*butane with *iso*butene was carried out in the same manner as with ethylene. The reaction occurs smoothly in spite of the ease with which *iso*butene polymerizes in the presence of boron fluoride, nickel and water. Octanes and dodecanes were the principal products of

the reaction. They were colourless and stable to both potassium permanganate and nitrating mixtures.

TABLE V.

| Compounds. | B.P. Range ° C. | Vol. Per cent. of Total Liquid Produced. |
|---|---|---|
| Pentanes . . . | 5–45 | 2 |
| Hexanes . . . | 45–75 | 19 |
| Heptanes . . . | 75–100 | 6 |
| Octanes . . . | 100–125 | 22 |

*iso*Pentane was alkylated with ethylene to the extent of 40 per cent. Paraffins were obtained as a water-white mixture. Alkylation of 2 : 2 : 4-trimethylpentane with ethylene did not proceed as readily at the temperatures employed as those reactions previously noted. From 5 to 10 per cent. of 2 : 2 : 4-trimethylpentane reacted with ethylene; however, some polymerization of ethylene occurred yielding unsaturated, high-boiling liquids.

Both normal and *iso*paraffins are alkylated with olefins in the presence of aluminium chloride, which is in contrast to boron fluoride. Paraffins from butane to dodecane have been alkylated, and the reaction seems to be a general one.[21] The first three members of the olefin series have been used to carry out the alkylation reaction, since side reactions complicate the mechanism. The three reactions which have been determined to take place when aluminium chloride catalyst is used are: (1) "autodestructive alkylation" whereby a paraffin splits to form a paraffin and an olefin, the latter reacting to alkylate another paraffin; (2) polymerization of the olefins and the splitting takes place yielding paraffins; (3) formation of aluminium chloride addition compounds yielding the characteristic reddish-brown layers of reaction mixtures denoting addition compounds. These three reactions take place simultaneously, but the extent of each is dependent on the individual hydrocarbons used and the experimental conditions.

The alkylation of paraffins with olefins at high temperatures and pressures was carried out by Frey and Hepp.[22] They found that at pressures ranging from 2500 to 4500 lb. to the square inch and temperatures of 950° F. propane and *iso*butane reacted with ethylene forming normal and *iso*-paraffins of the combined molecular weight of the two. In the alkylation of propane and ethylene the liquid produced contained 25 per cent. of normal pentane and 50 per cent. *iso*pentane. In addition, olefins and paraffins were formed ranging from $C_6$ to $C_9$ hydrocarbons. When reacting ethylene and *iso*butane, hexanes were the chief product, representing about 57 per cent. of the gasoline fraction. Of the hexane fraction about 80 per cent. was 2 : 2-dimethylbutane having an octane rating of 94·5. Other hydrocarbons produced during the reaction were pentenes, normal and *iso*pentanes, heptenes, heptanes, octenes, octanes and nonanes.

It was stated [22] that: "While thermal polymerization of gaseous olefins to motor fuel ordinarily leads to the formation of a complex mixture of hydrocarbons, the use of favourable alkylation conditions makes possible

the synthesis of *iso*paraffins of varying structure and molecular weight or volatility by the choice of suitable reactant paraffins and olefins. Such *iso*paraffins, particularly the more highly branched in structure, have high anti-knock ratings and possess high stability, calorific value and lead susceptibility. These characteristics are particularly desirable in aviation fuel. *iso*-Octane (2 : 2 : 4-trimethylpentane) is a now familiar example."

### 5. Alkylation of Aromatics and Phenols.

The alkylation reaction of cyclic structured organic compounds is an old one. Many catalysts have been used, particularly sulphuric acid and aluminium chloride. Relatively recently, olefins from cracked gases have been used as alkylating hydrocarbons.

The alkylation of aromatic hydrocarbons with ethylene, propene, butenes, pentenes, hexenes, etc., from cracked products in the presence of aluminium chloride yields derivatives consonant with the benzene, toluene and xylenes used. In the reaction of ethylene and benzene, 1 molecule of aluminium chloride uses 100 molecules to react forming ethylbenzene.

As a rule the alkylation reaction of the aromatics is one of substitution only; however, the rate of reaction is slower when the higher-molecular-weight olefins are used. These alkylation reactions of aromatics may lead to benzene, alkylated and condensed aromatics, arylated paraffins, olefins and *cyclo*paraffins, *cyclo*paraffinic aromatics and paraffins. Contact times and concentrations of the aluminum chloride are the deciding factors in alkylating reactions.

The alkylation of benzene with olefins [23] in the presence of sulphuric acid takes place with two other reactions competing for the substances present. These reactions are polymerization of the olefin, and the formation of esters. When 96 per cent. sulphuric acid is used, alkylation and ester formation occur, but not polymerization.

The mechanism of alkylation is thought to be by ester formation; the ester functions as the alkylating agent. Boron fluoride [24] has been used as a promotor with sulphuric acid for the production of mono-, di-, and tri-*iso*propyl benzenes. Further alkylation reactions have been found to occur when using butene-1, pentene, octene, nonene and dodecene as alkylating substances for benzene. Identical reactions have been found to occur when toluene and naphthalene are reacted with propene.

In the production of alkylated phenols for specific germicides from phenol and cracked gases and liquids with sulphuric acid starting materials, the intermediate sulphonated alkyl phenols are first formed, and this is hydrolysed under pressure to obtain the alkylated phenol product and sulphuric acid. These alkylated phenols may have homologues of cresol, resorcinol, hydroquinone, pyrogallol or naphthol produced in the same manner. This mode of synthesis makes available at reasonable cost products which have desirable characteristics for many uses. It is known that certain alkylated phenols are quite specific in germicidal action with regard to bacteria. Hexyl phenols appear to have maximum germicidal activity for *B. typhosus*, whilst heptyl and octyl phenols, of less germicidal value than hexyl phenol for this bacterium, are much more effective than hexyl phenol in killing *Staphylococcus dureus*. The mixed alkyl phenols

prepared from petroleum are therefore suitable for general germicides for a variety of bacteria. Similarly the crude butylphenols, together with oily polymers, are particularly suitable for horticultural sprays or wood impregnants. The production of these materials directly from petroleum fractions permits considerable saving in the cost and ease of preparation. Alkylated phenols are also useful as antioxidants in cracked gasoline in order to stabilize it against gum formation due to air in storage.

"The reaction of trimethylethylene with phenol[25] in the presence of sulphuric acid to make tertiary amyl phenol is particularly interesting, as this product is finding considerable use in the manufacture of oil-soluble phenolformaldehyde resins. In the case of trimethylethylene it is assumed that the reaction takes place to form an intermediate of tertiary amyl phenyl ether, which rearranges to form the tertiary amyl phenol. However, this ether has never been isolated. In the case of a secondary olefin, such as pentene-2, the ether formed is fairly stable, and only with heat does it rearrange to form the secondary amyl phenol. The primary ether, prepared by reacting *n*-butyl carbinyl chloride with sodium phenate, is very stable, and only with drastic treatment does it rearrange. It is extremely interesting to note that the rearrangement gives a secondary isomer rather than *n*-amyl phenol.

"*para*-Tertiary amyl phenol is interesting industrially because some of its properties differ so greatly from ordinary phenol. It is not hygroscopic, is insoluble in water and has a melting point above 82° C. It has practically no irritating action on the skin, and its phenol coefficient is approximately 60. When condensed with aldehydes it forms oil-soluble resins of the phenol formaldehyde type which are suitable for use in varnishes because of their colour stability on exposure to light and their durability.

"When *para*-tertiary amyl phenol is nitrated, the dinitroderivative is the predominating product, and both nitro-groups appear to be in *ortho* positions to the hydroxyl group. This arrangement would be expected, since further nitration of either *ortho*- or *para*-mononitrophenol yields 2 : 4-dinitrophenol and in *para*-tertiary amyl phenol the 4-position is already occupied by the amyl group."

### 6. Cyclization of Paraffins.

There is a very beautiful reaction called cyclization of paraffin hydrocarbons; *i.e.* catalytically converting normal hexane, heptane and octane into benzene, toluene and xylenes respectively, with hydrogen as a by-product with yields almost theoretical.

The lower-boiling hydrocarbons in petroleum, particularly those from the Pennsylvania, Mid-Continent, Michigan and other fields, are predominantly straight-chain paraffins. By catalytic cyclization at 500° C. and atmospheric pressure these hydrocarbons may be converted into the corresponding aromatic hydrocarbons with almost theoretical yields, which heretofore have been obtainable chiefly from coal tar. These hydrocarbons are the basis of a large number of synthetics aside from motor fuel such as explosives, dyes and medicinals.

At the moment the aromatic hydrocarbons are not so good for aeroplane use, although there are some tests which indicate that they might become

useful for that purpose. They are excellent blending hydrocarbons to increase the octane rating of gasolines. The cyclization of paraffins in petroleum to aromatics gives another enormous source of supply of high anti-knock motor fuels.

### 7. Isomerization.

The gasolines derived from crude oil are predominantly paraffinic of straight-chain character. As is well known, long straight-chain paraffin hydrocarbons are highly detonating in a motor, whilst the branch chain make excellent motor fuels. It is highly desirable to isomerize the knocking paraffins into the branch-chain type, due to their slow burning in an automotive cylinder. The octane rating of a number of paraffin hydrocarbons are given in Table VI.

Table VI.

| Hydrocarbon. | Octane Rating. |
|---|---|
| Methane | 125+ |
| Ethane | 125+ |
| Propane | 125+ |
| Butanes: | |
| *iso*Butane | 99 |
| *n*-Butane | 91 |
| Pentanes: | |
| 2 : 2-Dimethylpropane | 83 |
| *iso*Pentane | 90 |
| *n*-Pentane | 64 |
| Hexanes: | |
| 2 : 2-Dimethylbutane | 95 |
| 2 : 3-Dimethylbutane | 95 |
| *n*-Hexane | 59 |
| Heptanes: | |
| 2 : 2-Dimethylpentane | 93 |
| 2 : 3-Dimethylpentane | 85 |
| 2 : 4-Dimethylpentane | 90 |
| 2-Methylhexane | 64 |
| *n*-Heptane | 0 |
| Octanes: | |
| *n*-Octane | −28 |
| 2 : 2 : 3-Trimethylpentane | 101 |
| 2 : 2 : 4-Trimethylpentane | 100 |

As a picture of rearranging the carbon–carbon linkage in the molecules, the process of isomerization has developed where, by the use of a catalyst, normal hydrocarbons are converted into *iso*-. One of the key hydrocarbons in building up structurally of high branch-chain paraffin hydrocarbons of high anti-knock value is *iso*butane. The percentage of *iso*butane as such is relatively low in natural and cracked gases and natural gasoline, however, the normal compounds are much higher, hence it is desirable to rearrange the normal butane and butenes into the *iso*-compounds. This has been accomplished.

The catalytic isomerization of normal butane to iso by the use of aluminium chloride at 175° C. and 35 atmospheres pressure was shown.[26] Another research using aluminium bromide at room temperature and 3 atmospheres pressure during a two months time period produced 78–82 per cent. *iso*-

butane from normal at equilibrium conditions.[27] Pentane isomerized to *iso*pentane to the extent of 55·9 per cent. at room temperature in the presence of aluminium bromide.[28] *iso*Hexanes were produced by the catalytic action of aluminium chloride upon normal hexane.[29]

When normal heptane[30] was studied, it was found that the temperatures of isomerization and polymerization were very close to each other. The amount of isomerization depends on the catalyst used, 85 per cent. of the heptane isomerized at 420° C., and 3 hours heating time at 70 atmospheres pressure in the presence of molybdenum sulphide. Other catalysts used were zinc chloride, aluminium chloride and copper oxide. A 4 per cent. yield of 2-methylhexane[31] was obtained when normal heptane was treated with aluminium chloride at 100° C. At a later time[32] the following products were identified after reacting normal heptane with aluminium chloride at 96° C. (90° C. in the still head). The percentages are based on 100 parts of heptane reacting; pentanes and below, 64·6 per cent.; 2-methylpentane, 3·4; 3-methylpentane, 2; hexane, 0·4; 2-methylhexane, 1·2; 3-methylhexane, 1·6; polymerization products were also formed and no naphthenes.

Isomerization[33] of 1-butene to 2-butene takes place in the presence of phosphoric acid catalyst. The reaction is carried out at pressures varying from 2·45 to 8·2 atmospheres with contact times of 4·25 to 17 hours. The temperatures range from 99° to 325° C. The optimum conditions for the production of 2-butene from 1-butene were a temperature of 249° C.; pressure of 7·8 atmospheres and 2·75 hours reaction time. The yield of 2-butene was "100 per cent. by volume." There was some evidence that an equilibrium exists in the rearrangement, since a four-fold increase in contact time caused little change in the per cent. conversion of 1- into 2-butene. On passage through pure *ortho*-phosphoric acid at 100° C., *trans*-2-butene was converted to the extent of 6·6 per cent. into 1-butene, 6 per cent. into *cis*-2-butene. Partial isomerization of 1- into 2-butene was also obtained in the presence of perchloric acid, aqueous zinc chloride solutions and benzene sulphonic acid.

Pentenes also have been shown to isomerize[34] in the same manner as the butanes—that is, 2-pentene is formed from 1-pentene and vice versa. The reaction takes place between 550° and 600° C., and when the contact times are from 8–19 seconds, the reaction products contain $\frac{1}{4}$ to $\frac{3}{4}$ of the isomeric pentene. Later it was reported that these isomerizations occurred above 580° C., but neither of the normal pentenes isomerized to the branched-chain *iso*propyl ethylene.

### 8. Ethers, Ketones and Alcohols.

Chemical derivatives from cracked gases such as ethers, ketones, and alcohols are being produced which are usable as motor fuel as well as other industrial uses. The ethers (except ethyl ether) are excellent anti-knock fuels particularly from a blending standpoint. Isopropyl ether, having an octane rating of 101 is potentially available at the rate of over 10 million barrels per year. As an auxiliary 100 octane fuel for airplane use, 40 per cent. is blended with aviation gasoline and 3 c.c. tetraethyl lead, this makes available over 25 million barrels of 100 octane gasoline yearly from the cracked gases in the refineries of the world.

Other branched chain ethers, such as methyl tertiary butyl, methyl tertiary amyl, ethyl tertiary butyl, ethyl tertiary amyl, iso-propyl tertiary butyl, normal propyl tertiary butyl, and secondary butyl tertiary butyl have octane ratings over 100. The availability of these ethers is a function of the size of the hydrocarbon chains present in the compound, the volumes decreasing with the increasing molecular weight of hydrocarbon employed. Isopropyl ether may be used to augment the *iso*-octane fuels available, the ether supplying the front and volatility lacking in *iso*-octane.

The octane ratings and physical properties of a number of mixed ethers are given in Table 7.

TABLE VII.

| Ether. | Boiling Point °C. | Spec. Grav. | | Non-Leaded. | Octane Blending Value, 25% Blend in 74 Octane Aviation Gasoline Leaded, 1 c.c. TEL/Gal. |
|---|---|---|---|---|---|
| | | | A.P.I. | | |
| Di-*iso*propyl . . | 68·4 | 0·722 | 64·5 | 101 | 105 |
| Methyl*iso*propyl . | 31·5 | 0·735 | 61·0 | 73 | 90 |
| Methyl*tert.*-butyl . | 55·3 | 0·735 | 61·0 | 111 | 106 |
| Methyl*tert.*-amyl . | 86·0 | 0·754 | 56·2 | 108 | 108 |
| Ethyl*iso*propyl. . | 54·0 | 0·720 | 65·0 | 75 | 87 |
| Ethyl*sec.*-butyl . | 81·3 | 0·738 | 60·2 | 63 | 73 |
| Ethyl*tert.*-butyl . | 72·3 | 0·736 | 60·7 | 115 | 114 |
| Ethyl*tert.*-amyl . | 101·5 | 0·759 | 54·9 | 112 | 106 |
| *iso*Propyl*tert.*-butyl . | 87·6 | 0·736 | 60·7 | 112 | 118 |
| *n*-Propyl*tert.*-butyl . | 98·0 | 0·747 | 57·9 | 103 | 106 |
| Di*sec.*-butyl . . | 114·0 | 0·756 | 55·7 | 95 | — |
| *sec.*-Butyl*tert.*-butyl . | 114·0 | — | — | 106 | 105 |
| *tert.*-Butyl-*n*-butyl . | 123·0 | 0·758 | 55·2 | 81 | 92 |
| *tert.*-Butyl-*n*-amyl . | 143·0 | 0·770 | 52·3 | 63 | 80 |

Methyl ethyl ketone and acetone have also been found to have good lead susceptibility and high anti-knock value. Acetone may be produced from the propene present in cracked gases and methyl ethyl ketone is manufactured from butanol-2, which may be obtained from the butenes present in cracked gases.

Ketones have been suggested as a blending agent in the manufacture of high octane aircraft fuels. The particular blending agent tested in a Rolls-Royce engine was a mixture of ketones characterized by physical properties different from the more general alcohols. When this mixture of ketones was blended with aromatic and non-aromatic fuels in varying percentages and with varying tetraethyl lead additions, the response was found to depreciate as the gasoline in the mixture was increased, indicating that the ketones had better tetraethyl lead response.

The advantage particularly of these high octane fuels in addition to *iso*-octane rests in the take-off of the plane from the ground with a heavier load than it can lift otherwise. In planes actually tested with motors that were not specifically designed for 100 octane fuel, the take-off load was increased from 10 to 20 per cent. with an increased power output of 15 to 30 per cent.

Alcohols have been produced from cracked products ranging from ethyl to cetyl. The most important ones at the present are ethyl, *iso*propyl,

butyl and amyl alcohols. The volume of ethyl alcohol produced from cracked gases during 1936 in the U.S.A. was over 10 million gallons. The alcohols are primarily used as solvents, intermediates and medicinals. The potential supply of alcohols from present world refining of crude oil is over 200,000,000 barrels. Alcohols have good anti-knock and blending properties for motor fuel use.

The octane ratings, blending values and tetraethyl lead susceptibilities of methyl, ethyl, normal, iso, secondary, and tertiary butyl alcohols are shown in Table VIII.

TABLE VIII.

*Octane Blending Value and TEL Susceptibilities of Various Alcohols.*

| | Methyl.† | Ethyl. | *n*-Butyl. | *iso*-Butyl. | *sec.* Butyl. | *tert.*-Butyl. | Amyl. | *tert.*-Amyl. |
|---|---|---|---|---|---|---|---|---|
| Octane Number: CFR Motor Method: Straight | 98·0 | 99·5 | 87·5 | 87·5 | — | 100+ (*iso*-Octane +3 c.c. TEL/Gal.) | 77·5 | 100+ (*iso*-Octane +0·2 c.c. TEL/Gal.) |
| Blended 50% with 70 Octane Straight-Run Gasoline* | 89·0 | 88·5 | 81·5 | 82·0 | 85·0 | 83·5 | 72·5 | 84·5 |
| +1 c.c. TEL/Gal. | 91·5 | 89·0 | 84·5 | 84·5 | 87·0 | 91·0 | 79·0 | 89·5 |
| +2 " " | 93·5 | 89·0 | 86·5 | 86·0 | 88·5 | 95·0 | 82·0 | 92·0 |
| +3 " " | 95·0 | 89·5 | 87·5 | 87·0 | 89·0 | 97·0 | 83·5 | 92·5 |
| +4 " " | 96·0 | 89·5 | 88·5 | 87·0 | 89·5 | 99·5 | 84·5 | 93·0 |
| Army Method: Straight | — | — | — | — | — | 100+ (*iso*-Octane +2·5 c.c. TEL/Gal.) | — | 100+ (iso-Octane +0·5 c.c. TEL/Gal.) |
| Blended 50% with 70 Octane Straight-Run Gasoline* | 85·5 | 86·5 | 80·5 | 84·5 | — | 85·5 | 72·5 | 85·0 |
| +1 c.c. TEL/Gal. | 87·5 | 87·0 | 83·5 | 86·0 | — | 93·0 | 78·0 | 91·0 |
| +2 " " | 88·0 | 87·0 | 85·0 | 87·5 | — | 97·0 | 80·5 | 93·5 |
| +3 " " | 88·0 | 87·5 | 85·5 | 88·5 | — | 99·0 | 82·5 | 94·0 |
| +4 " " | 88·0 | 87·5 | 85·5 | 89·0 | — | 100+ | 84·0 | — |

* California straight-run gasoline.
† Blend contained 40 per cent. methyl and 10 per cent. ethyl alcohol.

It will be noted that, although a number of the alcohols affect an appreciable increase in octane number, their tetraethyl lead susceptibilities vary over a wide range. The tertiary butyl and tertiary amyl alcohols show a lead susceptibility equal to or better than that of the straight-run base fuel.

In practice a 10 per cent. blend of ethyl alcohol with gasoline has shown that the fuel consumption is at least 4 per cent. higher than with gasoline alone. Comparative fuel tests give the results shown in Table IX.

TABLE IX.

*Comparative CFR Dynamometer Tests with 10 per cent. Alcohol–Gasoline Blend and Gasoline Alone.*

| Fuel. | Brake Horsepower. | Lb. Fuel/ B.h.p./Hr. | % Increase in Consumption. |
|---|---|---|---|
| Gasoline | 2·19 | 0·75 | — |
| 10% Alcohol–Gasoline Blend | 2·19 | 0·78 | 4·0 |

Aside from this increased fuel consumption with alcohol–gasoline blends, the use of alcohol introduces certain operating difficulties such as starting,

acceleration and vapour lock. The lower or water-soluble alcohols are difficult to blend with gasoline unless they are substantially anhydrous or unless a blending agent such as benzene, toluene or one of the higher alcohols (*n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, or *tert*-butyl) is used.

## 9. Oxidation.

The oxidation of paraffin hydrocarbons to produce alcohols, aldehydes and acids has been carried out experimentally and commercially. The direct oxidation of methane from natural gas to methanol is being carried out commercially in the U.S.

The use of high pressure and lower temperature promotes the yield of alcohols, but does not decrease the danger of explosion. It has been stated that oxidation of methane at 3000 lbs. per sq. in. pressure and 400° C. temperature is safe in the presence of less than 10 per cent. oxygen.[35]

Investigations among the paraffins have included the controlled direct oxidation of paraffins from methane to waxes. The oxidation of methane has been directed towards the formation of methyl alcohol, formaldehyde, carbon monoxide and acetylene.[36]

$$CH_4 + 0{\cdot}5\ O_2 \longrightarrow CH_3OH$$
$$CH_4 + 1{\cdot}0\ O_2 \longrightarrow HCHO + H_2O$$
$$CH_4 + 1{\cdot}5\ O_2 \longrightarrow CO + 2H_2O$$
$$2CH_4 + 1{\cdot}5\ O_2 \longrightarrow C_2H_2 + 3H_2O$$

The oxidation of ethane has been directed towards the formation of ethyl alcohol, acetaldehyde and acetic acid. However, some methyl alcohol is also formed.

Propane, butane and pentane oxidized under pressure with oxygen form alcohols, aldehydes, ketones and carboxylic acids. Propane [37] oxidized with oxygen at 2000 lb. per square inch and 300–350° C. forms a liquid containing methyl alcohol 22 per cent., ethyl alcohol 37 per cent., propyl alcohol 7 per cent., acetaldehyde and acetone 6 per cent., formic acid 1·5 per cent., and water 26·5 per cent. Formaldehyde [38] is obtained from propene and other hydrocarbons by oxidation in the presence of oxides of nitrogen. Investigations have included also the dehydrogenation [39] of butane to butene and the formation of fatty acids from waxy oils.

Oxidation of kerosene and gas oil gives a complex mixture of "crude aldehydes," useful as a denaturant. Gas oil [40] oxidized by air at 400° C. and 300 lb. per square inch pressure produces methyl alcohol, ethyl alcohol, allyl alcohol, dimethyl acetal, acetaldehyde, acetone and acetic acid.

The typical oxidation reactions of paraffins can be summarized as follows:

| | |
|---|---|
| $R{-}CH_3 + 0{\cdot}5\ O_2 \longrightarrow R{-}CH_2OH$ | Primary alcohols. |
| $R{-}CH_3 + 1{\cdot}0\ O_2 \longrightarrow R{-}CHO + H_2O$ | Aldehydes. |
| $R{-}CH_3 + 1{\cdot}5\ O_2 \longrightarrow R{-}CO_2H + H_2O$ | Carboxylic acids. |
| $\begin{matrix}R\\R\end{matrix}\!\!>\!CH_2 + 0{\cdot}5\ O_2 \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>\!CHOH$ | Secondary alcohols. |
| $\begin{matrix}R\\R\end{matrix}\!\!>\!CH_2 + 1\ \ O_2 \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>\!C=O + H_2O$ | Ketones. |

Investigations among the cyclic hydrocarbon fractions have included the oxidation of *cyclo*hexane to adipic acid [43] and the vapour phase oxidation [41, 42] of benzene, toluene and naphthalene.

Oxidized naphthenic and aliphatic hydrocarbons are claimed to be insecticides and fungicides.

In Germany the oxidation of paraffin waxes to fatty acids for soap-making and fats for food is going on industrially.

## 10. Halogenation.

The halogenation of hydrocarbons derived from natural gas or petroleum has developed a number of useful products such as ethylene dichloride, ethylene trichloride, propylene dichloride, amyl chlorides, and chlorhydrins which are source materials for many other derivatives. The chlorination of hydrocarbons has been renewed.[44]

Chlorination of natural gas produces substitution products of methane, including methylene chloride, chloroform and carbon tetrachloride, finding use as solvents. Methyl chloride can be produced also, and finds use as a methylating agent and refrigerant. The analogous methyl bromide has been proposed as a fire extinguisher and otherwise.[45]

Treatment [46] of 1-pentene and 1-hexene with bromine and then with alkalies gives the corresponding acetylenes, useful as intermediates in the manufacture of aldehydes, ketones, acids, hydrocarbons and other derivatives.

Ethylene from cracked gases is one of the base materials used in the production of Thiokol. Ethylene is chlorinated to ethylene dichloride, and treated with a sodium-sulphide complex. These high-polymer condensation products are competitive with natural rubber and synthetic rubbers for use as hose, ceiling or floating roofs, moulded articles, cable insulations, etc.

In the chlorination of normal and *iso*pentane by the Sharples Solvents Corporation [47] in the vapour phase " the present plant is capable of feeding 22 tons of chlorine per day continuously into a 60-mile-per-hour stream of hot pentane vapour. 100,000 gallons of pentanes pass through the reaction zone every day, but at any given moment only 3 gallons of pentanes are present in that zone. Not more than 8 ounces of free chlorine are in contact with the pentanes at any given moment."

A number of amyl alcohols have been obtained from chlor-derivatives of normal and *iso*pentanes.

" The esters of a large number of acids can be made from Pentasol, a mixture of the synthetic amyl alcohols. By far the most important of these is Pent-acetate, the acetic acid ester of Pentasol. It is used in large quantities in the lacquer industry.

" Numerous other amyl derivatives are made from mixed amyl chlorides. One of these is amyl mercaptan. Its use as an odorant in natural gas is increasing rapidly. Seven-tenths of a pound of amyl mercaptan added to 1,000,000 cubic feet of gas will impart a sufficient odour to warn that unburned gas is escaping somewhere in the house. Breaks in pipe-lines as much as 7 feet underground have been located by its use.

" Amyl chlorides under proper conditions react with ammonia to form monoamyl-, diamyl- and triamyl-amines. The boiling points of the three are sufficiently far apart to permit satisfactory separation by distillation. This is not the case with the lower aliphatic amines, such as methylamine,

where the boiling point of the mono-derivative is higher than that of the di-, and the tri- is about the same as that of the mono-. The amines offer a convenient starting material for a host of interesting syntheses.

"The amines are strong bases, a molar solution of monoamylamine having a pH of 11·67, compared with 11·62 for one molar ammonium hydroxide solution. Monoamylamine is completely miscible with water, and is a powerful organic solvent of about the same order of magnitude as pyridine. Diamylamine is only slightly soluble in water, whilst triamylamine is practically insoluble.

"The amines enter into all the typical reactions of amines. They can be condensed with aldehydes, ketones and oxides. The hydrogen of monoamylamine and diamylamine is replaceable with metallic sodium. Monoamylamine with metallic sodium reacts on warming, one hydrogen atom being replaced by sodium, giving sodium amyl amide. The amines also react with phosgene, urea, cyanic acid, thiocyanic acid and *iso*cyanates to give ureas and thioureas. Being strong organic bases, the amylamines react readily with fatty acids forming organic soaps. These soaps have excellent emulsifying properties.

"Diamylnitrosamine, prepared by reacting nitrous acid with diamylamine, is a high-boiling liquid which has the ability to markedly inhibit the corrosion of $H_2S$.

"Other interesting derivatives of the amyl chlorides are those formed by their reaction with benzene, naphthalene, aniline, phenylenediamines, diphenylamine, benzylamines, phenol, cresols and other related compounds. It is thus possible to prepare a whole series of mixed aliphatic-aromatic derivatives which in turn can serve as raw materials for other syntheses.

"In hydrolysing the mixed amyl chlorides, some of them decompose to form amylenes. Perhaps all of the five possible amylenes are formed during the hydrolysis, but apparently a re-arrangement takes place, and the two main products obtained are pentene-2 and trimethylethylene. It has been found that pentene-2 is the stable configuration for the 5-carbon straight-chain olefin, and the pentene-1 can be rearranged by heat to pentene-2. Likewise, *iso*propyl ethylene and unsymmetrical methyl ethyl ethylene apparently rearrange to the stable configuration of the branched chain, trimethylethylene.

"The dichlorides of the pentanes form constant-boiling mixtures with water boiling between 95° and 100° C. These mixtures contain about ten parts dichlorides to one part water. Distillation of 2 : 3 dichloro-2-methylbutane with water is accompanied by the production of considerable hydrogen chloride but 2 : 3-dichloropentane can be distilled with water substantially without decomposition. However, it is subject to the same sort of slow hydrolysis that has been observed in carbon tetrachloride.

"The dichloropentanes are splendid solvents for rubber, grease, resins and bituminous materials. Their comparatively high flash-point (110° F.) minimizes the fire hazard. Because of the relatively low evaporation rate, they are useful in paint and varnish removers, and for the final cleaning of metal surfaces to be electro-plated. They are also useful for certain types of soil fumigation.

"Thus, from the two-pentanes a large variety of commercially important synthetic organic chemicals are being produced. Numerous other

derivatives can be made from the available amyl chlorides, alcohols and amylenes. The same chlorination principles are applicable also to other hydrocarbons, and accordingly the number of similar products containing other than five carbon atoms which could be made in a similar manner is almost unlimited."

## 11. Solvent Extraction of Gasolines.

Straight-run gasolines contain predominantly straight-chain paraffins, small percentages generally of aromatics, with olefins sometimes present. Cracked gasolines also contain varying percentages of these groups. A chemical analysis of cracked motor fuels is shown in Table X.

Table X.

| Hydrocarbons, %- | N. Kansas Topped Crude Oil. | Kentucky Fuel Oil. | Smackover Heavy Crude Oil. | N. Texas Fuel Oil. | Lose Soldier Wyoming Crude Oil. | Spindle Top Texas Crude Oil. |
|---|---|---|---|---|---|---|
| Unsaturates . . | 16·1 | 14·4 | 14·7 | 16·0 | 11·7 | 14·7 |
| Aromatics . . | 17·8 | 22·5 | 27·5 | 18·6 | 15·9 | 17·3 |
| Naphthenes . . | 12·8 | 10·0 | 21·2 | 11·7 | 14·5 | 32·6 |
| Paraffins . . | 53·3 | 53·1 | 36·6 | 33·7 | 57·9 | 35·4 |

Solvent extraction by the Edeleanu sulphur dioxide extraction process segregates the low octane fraction or raffinate from the high octane fraction or extract. The raffinate may be cracked to yield high octane gasoline. It has been estimated that if the 650 million barrels of motor fuel produced in the world (estimated 1937 production) were solvent extracted, 130 million barrels of gasoline having an octane rating of 90 or over would be produced.

The gasoline solvent extraction process works at low temperatures

Table XI.

*Sulphur Dioxide Solvent Extraction.*

| | Charging Stock. | Gasoline Produced. | |
|---|---|---|---|
| Sulphur Dioxide used, % by Volume . | — | 40 | 40 |
| Extraction Temperature, ° F. . . | — | 0 | −60 |
| Yields, % by Volume . . . . | — | 12·5 | 9·1 |
| Gravity, ° A.P.I. . . . . | 53·1 | 36·7 | 32·2 |
| Octane Number, C.F.R.M. . . . | Below 41 | 82·6 | 91·0 |
| % by Volume . . . . . | 9·5 | 70·7 | 89·1 |
| Unsaturates and Aromatics: | | | |
| Naphthenes, % . . . . | 15·6 | 7·3 | 3·4 |
| Paraffins, % . . . . . | 74·9 | 22·0 | 7·5 |
| Sulphur, % . . . . . | 0·03 | — | 0·10 |
| A.S.T.M. Distillation: | | | |
| I.B.P., ° F. . . . . | 225 | 243 | 255 |
| 10% . . . . . | 256 | 271 | 279 |
| 50 . . . . . | 301 | 309 | 314 |
| 90 . . . . . | 359 | 362 | 364 |
| E.P., ° F. . . . . | 397 | 412 | 414 |

ranging from 0° to — 60° F., and the yield of high-octane fuel has been shown to be a function of the temperatures used.

Table (XI) shows a typical solvent extract which used 40 per cent. of sulphur dioxide and temperatures of 0° and — 60° F.

Blending values of the extracts, especially the high-octane ones, compare favourably with *iso*-octane; the data are shown in Table XII.

TABLE XII.

*Octane Numbers of Various Blends of Extract and iso-Octane with 63·4 Octane Straight-Run Gasoline.*

| Per cent. Blended. | Octane Number. | | |
|---|---|---|---|
| | Extracts. | | *iso*-Octane. |
| 100 | 91·1 | 98·2 | 100 |
| 75 | 83·1 | 86·5 | 88·5 |
| 50 | 77·5 | 79·0 | 79·7 |
| 25 | 70·0 | 71·5 | 71·0 |
| 0 | 63·4 | 63·4 | 63·4 |

## 12. OLEFINS AS GROWTH INDUCERS.

The unsaturated gases and liquids or their derivatives from cracked products have found important uses in ripening of fruits, as growth promoters, and for maturing potatoes and nuts.

Artificial ripening of citrus fruits began by exposing unripened citrus fruit to the fumes from an ordinary kerosene burner. It was found that exposure to these gases in comparatively air-tight rooms resulted in the destruction of the chlorophyll of the fruit. Later investigations showed that ethylene in the gases was responsible for the destruction of the natural green colouring matter in fruits.

The present treating in fruit-packing houses consists in storing fruit in rooms in the presence of ethylene or propene, maintained at temperatures of 70–75° F. with about 100 per cent. humidity. Unfortunately, this atmosphere is quite conducive to the growth of spores and various fungus diseases which are quite costly to the packer. Respiration rates of the fruits in the presence of ethylene are increased almost 100 per cent. at exposure times of 36–100 hours. This makes the fruit more prone to disease due to its lowered vitality. The blanching action of the ethylene does not continue after the fruit leaves the colouring-room, and it is thought that it is due to the absorption of ethylene by the oils and waxes of the skin. This action is often very slow, depending on the degree of ripeness of the original fruit.

Further uses of ethylene and propene have been in the stimulation of potato growth and transformation of starch into sugar. The effect on growth has been to bring certain vegetables and fruits to full maturity in a shorter growth season.

It has been shown that butenes have a similar effect in shortening the production season of such trees as walnut, peach, apple, pear, apricot, plum, prune and cherry. In periods when the season is too short to allow

the full maturing due to winter weather being so prolonged that flower formation and fruit setting are delayed, butene may be used to hasten the growth period. It is claimed [48] that this process is one which stimulates growth and produces uniform fruiting. The procedure which has been adapted to plant treatment consists of enclosing the trees in tents or gas-tight covers for about two weeks before the normal or desired leafing, *i.e.*, start of the growth cycle. Butene is then released inside the tent until the ratio is about one part to 100,000 parts of air, maintaining the temperature between 60° and 100° F. The length of treatment is from one to two hours.

A method [49] for eliminating packing-house colouring-room procedures has been to utilize butenes, pentenes, hexenes and heptenes which are normally present in cracked gasoline. Additional products of the unsaturated hydrocarbons derived from cracked products such as ethylene di-iodide, ethylene chlorohydrin, propene, chlorohydrin, also ethylene iodohydrin, ethylene butyrohydrin, ethylene acetohydrin and ethylene formohydrin, are also used as agents for furthering the ripening of fruit.

The peel of the green fruit which contains oil-soluble waxes absorbs the olefin or olefin derivative, and destroys the chlorophyll. The particular advantage in using such liquids as those mentioned lies in the fact that they are absorbed in sufficient quantity to continue their ripening action after being removed from the liquid, and upon storage under normal conditions the ripening is complete. This procedure eliminates the colouring-room treatment, which is devitalizing and quite costly due to hastening of rot.

The germination of dormant potatoes [50] has been brought about by both dipping and soaking the tubers in ethylene chlorohydrin solution. The procedure necessary has depended on the variety of tuber and on the stage of dormancy. It is reported [51] that the use of ethylene chlorohydrin as well as that of propene chlorohydrin for the germination of potatoes is practicable.

The use of petroleum derivatives in accelerating the growth and maturity of plant and tree life is finding more applications.

### 13. Olefins as Anæsthetics.

Purified olefin gases, particularly ethylene and propene, have found application in the field of anæsthesia in surgery. Their use has been advisable especially in cases where the patient could not be subjected to the nausea succeeding the use of ethyl ether.

Characteristics of ethylene anæsthesia are complete insensibility to pain before complete anæsthesia is established, no smothering and its consequent struggle, complete relaxation without the attendant decrease in heart action, and regular respiration without cyanosis. The induction of anæsthesia is pleasant; a slight hysteria only is observed before complete insensibility. The nausea so definitely marked in ethyl ether anæsthesia is only noticeable to a slight degree with ethylene or propene. The next meal is not interfered with in any way. There is no evidence of harmful after-effects, and its use is recommended for children, diabetics, in old age, in advanced arteriosclerosis, in high cerebral pressure, in operations on the brain, in major operations and in obstetrics.

All four hydrocarbons—ethylene, propene, butene and pentene—were found to have anæsthetic properties; their potencies are given on the basis of ethylene in 90 per cent. concentration being: [52] propene = 2·25, butene = 4·5 and pentene = 15. Their concentrations which produce anæsthesia are ethylene = 90 per cent.; propene = 40 per cent.; butene = 20 per cent.; and pentene = 6 per cent. Butene and pentene produced a marked excitement stage in anæsthesia.

Propene was recommended for further consideration as an anæsthetic, since it failed to cause any nervous symptoms.

Butene and pentene were markedly toxic in concentrations above those mentioned for anæsthesia, and this was due to respiratory failure, since their chief toxic action is on the respiratory centre. Additional toxic action may have been on the heart.

## 14. Other Processes Contributing to Efficient Uses of Petroleum Products.

Other products from petroleum have found uses in metallurgical industries for pickling inhibitors, quenching metals and in the preparation of blooming agents for lubricating oils. These materials are derived from such products from oil refining as sludge oils and residues.

When the "sludge oil" is used as a pickling inhibitor,[53] the acid is neutralized and the alkaline extract removed. The remaining oil is treated with acid and an alkali salt which removes the resulting acid oil nitrogen base, which is further hydrolysed and salted. When prepared in this manner the inhibitor is not disagreeable in odour and does not adhere to the metals being prepared for galvanizing or other finishing. It reduces the amount of metal lost by inhibiting the action of the pickling acid on the surface of the metal.

Another interesting development is the use of chemically treated cracked residues for the production of quenching oils. These already cracked products have a great thermal and oxidation resistivity to hot steels during quenching operation.

Many lubricating oils produced by nature do not have the "desirable" bloom useful for marketing purposes, hence bloom-imparting substances have been developed. Bloom-imparting material [54] is obtained by treating a cracked residue with acid containing 60–80 per cent. sulphuric acid and removing the sludge thus formed. The tar remaining after acid treatment is vacuum distilled in order to remove the waxes and lighter constituents. The bloom constituent is derived from the pitch-like substance which remains. The lubricating oil deficient in bloom is treated with from 0·2 to 4·0 per cent. by weight of the pitch to give a bloom to the oil. Coke from the cracking process is also used as a blooming agent by passing the lubricating oil through a column of coke.

Hydrogen sulphide from cracked gas is used to manufacture sulphuric acid. The cracked gas is treated with sodium phenolate, removing the hydrogen sulphide from the other gases present. The hydrogen sulphide is oxidized to sulphur trioxide, which is then absorbed by a solution of sulphuric acid. This process, which is in operation at the Standard Oil Company El Segundo refinery in California, has a capacity of 100 tons per

day of 100 per cent. sulphuric acid. This is more than enough to supply the needs of their own plant, and the remainder is sold to chemical companies in that vicinity. Besides eliminating the air pollution due to sulphur dioxide present in Los Angeles Basin, they have been able to polymerize 13 million cubic feet per day of cracked gases into motor fuel which is free from sulphur. By the removal of hydrogen sulphide in the cracked gas, the production of mercaptans in the polymer gasoline was prevented. Another will be producing 60 tons a day of 100 per cent. sulphuric acid from the hydrogen sulphide present in refinery gas. Therefore, three conservation forces have resulted of: (1) health, (2) sulphuric acid recovery, and (3) sulphurless polymer gasoline.

## 15. Conclusion.

The whole of the chemistry involved, shifting and changing in our industry of oil, has reached a high level, particularly in the past few years. The accelerated improvement rate is geometric rather than arithmetic. Exciting as the achievements of the oil industry have been in the better utilization and conservation of crude oil, one can look forward with assurance that the future will develop many new products which will have social benefits of great value to mankind.

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# THE CHEMICAL CONSTITUENTS OF PARAFFIN-BASE LUBRICATING OILS.*

By J. Müller and E. Neyman-Pilat.

It seems to be widely held that lubricating oils consist chiefly of three main groups of hydrocarbons, viz. aromatic, naphthenic and paraffinic. The aromatic constituents, without mentioning sulphur and oxygen-containing compounds, are probably responsible for the adhesive property of oils or the so-called "oiliness." On account of the unduly steep slope of viscosity with temperature and the ability to be oxidized, they are usually removed from oils by means of sulphuric acid or selective solvents. The naphthenic hydrocarbons are those which seem to be the chief constituents of lubricating oil fractions. Their properties depend on the number of rings present in a molecule. As has been shown by the work of Müller and Pilat,[1] the pure naphthenic hydrocarbons derived from naphthenic acids may, owing to the presence of side-chains, have very good lubricating properties, *e.g.* a flat viscosity temperature curve. This observation is, of course, contrary to the general belief that the advantageous properties of oils (as expressed by the viscosity index) are due to the presence of paraffinic hydrocarbons only. On the other hand, the problem whether there is a greater quantity of paraffinic hydrocarbons, or rather *iso*paraffinic hydrocarbons, in the lubricating oil fractions, is still an open question. So far nobody has succeeded in isolating the liquid paraffins from lubricating oils, and as the naphthenic hydrocarbons may possess those properties which are usually attributed to paraffinic hydrocarbons, there is no evidence of the presence of the latter in lubricating oil fractions.

In order to solve this problem, we have attempted the isolation of liquid paraffins from the lubricating oil fractions. The separation of a hydrocarbon mixture into chemical groups is not an easy one, as may be seen from the tremendous work devoted to this subject by the Bureau of Standards.[2] But in those cases where the separation by means of ordinary laboratory methods is impossible, the physical properties of the more or less purified and sharp fractions may help in elucidating their composition, as has been shown by the work of Waterman and his collaborators.[3] The following properties were determined on the oils investigated: densities by means of a pycnometer, the refractive indices on the Abbé refractometer. Molecular weights were determined by the cryoscopic method using naphthalene as a solvent. The elementary compositions and formulæ were calculated on the basis of very careful combustions by the method of Liebig. The molecular refractions "found" were calculated from the Lorentz–Lorenz formula, and the "calculated" from the elementary analysis using Eisenlohr's data, *i.e.* 2·418 for carbon and 1·100 for hydrogen. The kinematic viscosities were determined on the Vogel–Ossag viscometer, the values of viscosity indices calculated by the Dean and Davis method and

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TABLE I.

*Bright-stock from "Schodnica" Crude.*

| | Density. | | Refractive Index. | | Elementary Analysis. | | Molecular Weight. | Formula. | Molecular Refraction. | | Yield in Weight, %. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $d_4^t$. | $d_4^{20}$. | $n_D^t$. | $n_D^{20}$. | % C. | % H. | | | Calculated. | Found. | | |
| Starting material. | 0·951 15° C. | 0·948 | Too dark | — | 86·91 | 11·76 | 535 | $C_{38\cdot7}H_{62\cdot4}=C_nH_{2n-12}$ | 162·4 | — | 100 | Viscosity at 50° C., 5·0° E. |
| After $SO_3 + C_6H_6$ treatment. | 0·905 45° C. | 0·922 | | — | — | — | — | — | — | — | 51·3 | — |
| After nitrobenzene treatment. | 0·852 52° C. | 0·874 | 1·4825 23·5 | 1·4839 | — | — | — | — | — | — | 13·0 | — |
| After furfural treatment. | 0·852 48° C. | 0·872 | 1·4820 22·5 | 1·4830 | — | — | — | — | — | — | 11·6 | — |
| After the seventeenth pyridine extraction. | 0·8523 22·5° C. | 0·8545 | 1·4740 22·5 | 1·4750 | 85·90 | 14·21 | 649·4 | $C_{46\cdot9}H_{91\cdot6}=C_nH_{2n-1\cdot4}$ | 213·2 | 214·0 | 0·95 | — |
| After the twenty-fourth pyridine extraction. | 0·8524 19° C. | 0·8517 | 1·4748 19° | 1·4744 | 85·84 | 14·31 | 645·2 | $C_{46\cdot2}H_{91\cdot6}=C_nH_{2n-0\cdot8}$ | 212·5 | 213·1 | 0·41 | Pour point +19° C. |

the values of the " Polhöhe " from the Walther's formula.[4] The properties and compositions of all investigated fractions are included in Tables I, II, III, IV and V.

We started first with an acid-treated bright-stock from a Polish crude "Schodnica," which is of a typical paraffinic character. The material (possessing the properties as shown in Table I) has been first subjected to extraction with sulphur-dioxide–benzene mixture (3 : 1) to remove the bulk of aromatic constituents. This extraction was carried out four times at a temperature of 5° C. The resulting oil, 51 per cent. of the original sample, was further extracted with nitrobenzene. The mixture of 1 : 1 oil and nitrobenzene was heated above the critical solution temperature and separated after cooling to the room temperature. This procedure was repeated four times. In the course of extractions, owing to the increase in paraffinicity of the oil, the critical solution temperature rose in the following manner : 48°, 59°, 63° and 65° C. In order to remove as far as possible the aromatic and cyclic components, the raffinate obtained has been treated twice with furfural, then twice with pyridine boiling at 110–114°/730 mm., and twenty-two times with pyridine boiling at 113–114°/730 mm., *i.e.* almost free from water. The last raffinate obtained with the yield of 0·41 weight per cent. calculated on the bright-stock, ought, after all these treatments, to have contained the most paraffinic constituents of the oil investigated. The properties of this last fraction, however, especially the disagreement between the found and calculated molecular refractions, show clearly that it still contains some aromatic hydrocarbons.

With a view to obtaining better yields in the paraffinic fractions, oils of Pennsylvanian origin,* known as paraffin basis oils, have been subjected to a similar treatment. A heavy Pennsylvanian oil was extracted twice with nitrobenzene, the critical solution temperature being 59° and 64° C. The resulting raffinate was treated with furfural, but as this was a less selective solvent, a further extraction with nitrobenzene was undertaken. The critical solution temperatures after six extractions were 69°, 72°, 74°, 76°, 78° and 79° C., respectively. The subsequent extractions with pyridine and phenol–cresol mixture 3 : 1 ratio changed the properties of the raffinate to a slight extent only. The resulting oil was then treated continuously with acetone, which split the oil into two parts : a light-yellow solute in acetone with a higher percentage of hydrogen, and a dark raffinate containing hydrocarbons with a smaller percentage of hydrogen. This somewhat unexpected result of extraction may be explained as follows. Acetone is obviously a better solvent for cyclic than for paraffinic hydrocarbons, and the extract ought therefore to have a smaller content of hydrogen than the raffinate. Where, however, the treated oil consists of a mixture of hydrocarbons not differing greatly in their chemical structure—*i.e.* belonging practically to one chemical group—acetone tends to dissolve the hydrocarbons of smaller molecular weight. The selectivity of acetone seems to be much greater with regard to the size than to the character of molecules. This explains the unusual results that the raffinate may be heavier than the extracted oil.

As shown in Table II, the method of extraction does not lead to the further concentration of *iso*paraffins. Hence another method of separation has

* The Pennsylvanian oils were supplied by James B. Berry's Sons Co., Hamburg.

TABLE II.

*Pennsylvanian Oil No. ABVAJ.*

| | Density. | | Refractive Index. | | Elementary Analysis. | | Molecular Weight. | Formula. | Molecular Refraction. | | Yield in Weight, %. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $d_4^t$. | $d_4^{20}$. | $n_D^t$. | $n_D^{20}$. | % C. | % H. | | | Calculated. | Found. | | |
| Starting material. | 0·905<br>19·5 | 0·905 | 1·5025<br>19 | 1·5021 | 86·59 | 13·15 | 657 | $C_{47\cdot4}H_{85\cdot7}=C_nH_{2n-9\cdot1}$ | 208·9 | 214·3 | 100 | Viscosity at 50° C., 41·7° E. |
| After the second nitrobenzene treatment. | 0·881<br>24·5 | 0·884 | 1·4920<br>19 | 1·4916 | — | — | — | — | — | — | 61·5 | — |
| After furfural treatment. | 0·882<br>20·5 | 0·882 | 1·4900<br>20·5 | 1·4902 | — | — | — | — | — | — | 56·2 | — |
| After the seventh nitrobenzene treatment. | 0·878<br>17 | 0·876 | 1·4884<br>15 | 1·4864 | — | — | — | — | — | — | 36·4 | — |
| After pyridine treatment. | 0·878<br>17·5 | 0·876 | 1·4882<br>14 | 1·4858 | — | — | — | — | — | — | 33·3 | — |
| After phenol-cresol treatment. | 0·8774<br>18·5 | 0·8764 | 1·4885<br>16 | 1·4861 | — | — | 903 | — | — | — | 33·0 | — |
| Acetone extract. | 0·8669<br>20 | 0·8669 | 1·4828<br>17 | 1·4816 | 86·06 | 14·01 | 734·3 | $C_{52\cdot7}H_{103\cdot1}=C_nH_{2n-2\cdot3}$ | 239·7 | 241·4 | 16·5 | Pour point 6° C. |
| Acetone raffinate. | 0·8876 | 0·8876 | 1·4940<br>16 | 1·4924 | 86·24 | 13·70 | 1151 | $C_{82\cdot7}H_{156\cdot5}=C_nH_{2n-5\cdot3}$ | 372·1 | 376·5 | 16·3 | Pour point −3° C. |
| Crystals from acetone extract. | 0·8481<br>30·5 | 0·8553 | 1·4769<br>17 | 1·4757 | 85·64 | 14·30 | 632·6 | $C_{45\cdot1}H_{89\cdot5}=C_nH_{2n-0\cdot4}$ | 207·8 | 208·5 | 2·72 | Pour point 14° C. |
| Crystals from acetone raffinate. | 0·8813<br>18 | 0·8799 | 1·4909<br>17·5 | 1·4899 | 86·07 | 13·73 | 1051 | $C_{75\cdot4}H_{143\cdot2}=C_nH_{2n-7\cdot6}$ | 339·9 | 345·3 | 5·25 | Pour point 5·5° C. |

been applied. The extract and the acetone raffinate were each dissolved in 10 volumes of ethyl ether and chilled to − 70° C. The hydrocarbons precipitated in the form of crystals were filtrated and thoroughly washed with cold ethyl ether. In this way we obtained from the extract 16·5 per cent. and from the raffinate as much as 32·2 per cent. of constituents more paraffinic in character than the starting materials. As shown by the elementary analysis, the oil derived from the acetone extract may consist of a mixture of single-cyclic naphthenic hydrocarbons with a small amount of aromatics. The presence of the latter is reflected in the disagreement of molecular refractions.

From the observed data (Table II) we may conclude that the investigated Pennsylvanian oil does not contain liquid paraffins, unless in such small quantity as certainly cannot influence the physical properties of the oil. The course of the last acetone extraction showed, however, that there is a possibility of the presence of some liquid paraffins in lighter fractions. This observation led us to further investigations, in which we have used a much lighter Pennsylvanian oil (see Table III).

The oil investigated was extracted seven times with nitrobenzene, the critical solution temperature being 44°, 59·5°, 63°, 66·5°, 69°, 71·5° and 72·5° C. As the rise in critical solution temperatures after the last extraction amounted to 1° only, further extraction would apparently not lead to further separation. Thus, the raffinate was treated in a similar manner as before. A 10 per cent. solution in ethyl ether was cooled to − 70° C. and the hydrocarbons, precipitated in the form of crystals, were once more recrystallized from their solution in ether. As shown by the analysis (Table III), the second crystallization did not greatly affect the properties of the oil, which shows the separation by means of one crystallization to have been a very sharp one. The precipitated part of the oil is, of course, much richer in hydrogen than the corresponding filtrate.

After several unsuccessful extractions with different solvents, we succeeded finally in separating the previously recrystallized oil into two parts. The oil had been dissolved in a mixture of 250 c.cm. of petrol ether and 200 c.cm. of acetone. After cooling, the mixture separated into two layers, the upper containing a light oil A, and the lower a darker oil B. The oil A, as shown by the analysis, consists of much more saturated compounds than the oil B. In this case, however, as well as in those previously described, the values of molecular refractions indicate the presence of some small amounts of aromatic constituents. The probability of these being of a very similar character to the rest of the oil—*i.e.* possessing long paraffinic side-chains—makes it difficult to establish the presence of liquid paraffins. The oil A, in spite of the presence of aromatic hydrocarbons, has the formula $C_nH_{2n+0\cdot4}$, corresponding to a mixture of paraffins with other more cyclic or unsaturated compounds. Which type of paraffinic hydrocarbons is responsible for this formula has not been established. With regard to the high molecular weight and the pour point of 19·5° C. only, the presence of *iso*paraffins appears not unlikely.

The attempts described to isolate liquid paraffins from lubricating oils have shown in all three cases that the methods of extraction, as well as of crystallization, do not lead to the solution of this problem. The final products obtained consisted of a mixture of very similar hydrocarbons, which are no longer easily separable.

TABLE III.

*Pennsylvanian Oil No. 108.*

| | Density. | | Refractive Index. | | Elementary Analysis. | | Molecular Weight. | Formula. | Molecular Refraction. | | Yield in Weight, %. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $d_4^t$. | $d_4^{20}$. | $n_D^t$. | $n_D^{20}$. | % C. | % H. | | | Calculated. | Found. | | |
| Starting material. | 0·8783<br>15 | 0·8748 | 1·4891<br>19 | 1·4887 | 86·40 | 13·51 | 466 | $C_{33\cdot6}H_{69\cdot3}=C_nH_{2n-0\cdot7}$ | 149·8 | 153·7 | 100 | Viscosity at 50° C., 7·7° E. |
| After nitrobenzene treatment. | 0·865<br>17 | 0·863 | 1·4808<br>18 | 1·4800 | — | — | 621·7 | — | — | — | 39·6 | — |
| Product obtained by the first crystallization. | 0·8546<br>18·5 | 0·8536 | 1·4786<br>16 | 1·4770 | — | — | — | — | — | — | 10·1 | Pour point +13° C. |
| Product obtained by the second crystallization. | 0·8548<br>17 | 0·8527 | 1·4790<br>15 | 1·4770 | — | — | — | — | — | — | 9·9 | Pour point +14·5° C. |
| Product obtained from the filtrate. | 0·8658<br>17·5 | 0·8641 | 1·4810<br>16 | 1·4790 | 85·87 | 13·96 | 510·4 | $C_{36\cdot6}H_{70\cdot7}=C_nH_{2n-0\cdot8}$ | 166·1 | 166·4 | 29·5 | Liquid at −18° C. |
| Oil A. | 0·8267<br>28·5 | 0·8327 | 1·4642<br>26 | 1·4666 | 85·42 | 14·45 | 480·2 | $C_{34\cdot3}H_{69\cdot6}=C_nH_{2n+0\cdot4}$ | 158·4 | 159·9 | 1·2 | Pour point +19·5° C. |
| Oil B. | 0·8605<br>18 | 0·8591 | 1·4813<br>17 | 1·4801 | 85·77 | 14·26 | 553·1 | $C_{39\cdot2}H_{78\cdot3}=C_nH_{2n-0\cdot7}$ | 181·6 | 182·9 | 8·7 | Pour point +12·5° C. |

Mair and Schicktanz,[5] in their most valuable work on the chemical composition of a " water-white " lubricating oil from Mid-Continent crude, have found only one fraction corresponding to the formula $C_nH_{2n+x}$ in which the value of $x$ was greater than zero—namely 0·35. The values of the calculated and found refractions being for this fraction 129·7 and 129·5 and that of the specific dispersion 100·3,* a very small amount of aromatic compounds may be considered as being present. This example shows how difficult it is to separate the aromatic from the saturated compounds. The oil investigated by Mair and Schicktanz contains, however, some paraffinic hydrocarbons, but the melting point of the fraction not being given, it is difficult to know whether normal or *iso*paraffinic hydrocarbons are concerned.

In order to solve finally the question of the presence of *iso*paraffins in lubricating oils, we have once more made an attempt to isolate them, starting this time with a still lighter Pennsylvanian oil.† The properties of the oil as well as of the further products are shown in Table IV. The oil has been extracted seven times with nitrobenzene, the critical solution temperature being 44°, 48·5°, 51·5°, 54°, 55·5°, 57° and 58·5° C., respectively. The raffinate, which still contained a considerable amount of aromatic hydrocarbons, was left to crystallize from a 10 per cent. solution in ethyl ether at − 70° C. The product obtained with the yield of 7·5 per cent. (calculated on the Pennsylvanian oil) still contained some aromatic hydrocarbons, as may be seen from the disagreement in molecular refractions. Our previous experiments, as well as those of Mair and Schicktanz, have taught us that the methods of extraction do not lead to a quantitative separation of hydrocarbons which are very similar in their behaviour and physical properties.

It is a well-known fact that the presence of aromatics makes it difficult to calculate the composition of a mixture of hydrocarbons. As we have found the further removal of aromatics to be impossible, we have subjected the oil to a quantitative hydrogenation in order to change such aromatics into *cyclo*paraffinic hydrocarbons. The hydrogenation has been carried out under mild conditions in order to prevent any possible destruction of molecules. The oil dissolved in pentane has been hydrogenated in a small autoclave with nickel on an activated earth as a catalyst, at a temperature of 270° C. The initial pressure amounted to 120 atm. of hydrogen in each run. Although the substance was quite free from sulphur, so that the poisoning of the catalyst could not take place, the oil was found to be very resistant to hydrogenation. This might be explained as a consequence of the molecular structure of hydrocarbons. Such aromatics as still remained in the oil after all extractions and crystallizations might contain numerous paraffinic side-chains which render the hydrogenation more difficult. The course of hydrogenation has been controlled by measuring the refractive index of the oil after each run. Changing the catalyst after each hydrogenation, we succeeded finally, after seven runs, in getting the oil fully saturated. The analysis of the oil after the fifth and the seventh hydrogenations is

* This was calculated from the formula $\frac{n_F - n_C}{d} \cdot 10^4$ given by G. R. von Fuchs and A. P. Anderson, *Ind. Eng. Chem.*, 1937, **29**, 319; the authors have found that the specific refraction for pure paraffinic hydrocarbons amounts to 98·4, for naphthenic to 98·3, and for one-ring aromatics to 160–189.

† We have to thank Mr. O. Biskupski for his help in this part of our investigation.

TABLE IV.

*Pennsylvanian Oil No.* 106.

| | Density. | | Refractive Index. | | Elementary Analysis. | | Molecular Weight. | Formula. | Molecular Refraction. | | Yield in Weight, %. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $d_4^t$. | $d_4^{20}$. | $n_D^t$. | $n_D^{20}$. | % C. | % H. | | | Calculated. | Found. | | |
| Starting material. | 0·8685 20 | 0·8685 | 1·4851 17·5 | 1·4841 | — | — | 400 | — | — | 131·8 | 100 | — |
| After nitrobenzene treatment. | 0·8512 16·3 | 0·8484 | 1·4731 16·3 | 1·4716 | — | — | 507 | — | — | 167·3 | 36·1 | Pour point −7·5° C. Aniline point 117° C. |
| Product obtained by crystallization. | 0·8418 15·5 | 0·8384 | 1·4700 16 | 1·4684 | 85·48 | 14·03 | 480 | $C_{34\cdot2}H_{66\cdot6}=C_nH_{2n+0\cdot4}$ | 156·2 | 159·3 | 7·5 | Pour point 10° C. |
| After the fifth hydrogenation. | 0·8404 17 | 0·8382 | 1·4691 16 | 1·4675 | 85·39 | 14·46 | 479 | $C_{34\cdot1}H_{68\cdot2}=C_nH_{2n+0\cdot6}$ | 158·1 | 158·6 | ,, | Pour point 14° C. |
| After the seventh hydrogenation. | 0·8394 17 | 0·8372 | 1·4668 18 | 1·4660 | 85·59 | 14·52 | 479 | $C_{34\cdot1}H_{68\cdot9}=C_nH_{2n+0\cdot7}$ | 158·2 | 158·2 | ,, | Pour point 14·5° C. |

| Pennsylvanian oil No. 106. | Pennsylvanian oil No. 108. | Pennsylvanian oil No. ABVAJ | "Schodnica" bright-stock. |
|---|---|---|---|

shown in Table IV. The values of molecular refractions being in full agreement, we may consider the last product as completely saturated.

The value of $x$ in the formula $C_nH_{2n+x}$ amounts in the last product to 0·7. Assuming that this oil is composed of single-ring naphthenes and of

TABLE V.

*Kinematic Viscosity in Centistokes at :*

| | | 100° F. | 50° C. | 60° C. | 80° C. | 210° F. | Viscosity Index. | "Polhöhe." |
|---|---|---|---|---|---|---|---|---|
| "Schodnica" bright-stock. | After the seventeenth pyridine extraction . . | 141·04 | 79·30 | 51·96 | 26·11 | 15·41 | 116 | 1·600 |
| | After the twenty-fourth pyridine extraction . . | 149·68 | 84·77 | 55·43 | 27·66 | 16·37 | 118 | 1·578 |
| Pennsylvanian oil No. ABVAJ | After phenol–cresol treatment . . | 735·02 | 339·41 | 201·71 | 81·76 | 41·44 | — | 1·820 |
| | Acetone extract . | 287·90 | 144·07 | 88·74 | 40·19 | 21·52 | 97 | 1·830 |
| | Acetone raffinate . | 2,224·3 | 950·88 | 520·80 | 188·61 | 83·89 | — | 1·871 |
| Pennsylvanian oil No. 108. | After nitrobenzene treatment . . | 170·91 | 93·89 | 60·94 | 29·71 | 17·10 | 112 | 1·646 |
| | Product obtained by the first crystallization . . | 171·93 | 98·15 | 66·03 | 33·77 | 19·97 | 126 | 1·362 |
| | Oil A . . . | 38·94 | 25·15 | 18·29 | 10·74 | 8·04 | 153 | 1·255 |
| Pennsylvanian oil No. 106. | Starting material . | 45·36 | 27·79 | — | 10·66 | 6·97 | 102 | 1·704 |
| | After the seventh hydrogenation . | 36·86 | 23·72 | 17·25 | 10·29 | 6·74 | 138 | 1·223 |

paraffinic hydrocarbons of the same molecular weight only, the proportion of the paraffins would be 35 per cent. This value is, of course, the lower limit of the paraffin content, as the presence of more cyclic naphthenes would require for the same formula a higher percentage of paraffinic hydrocarbons. As the pour point of the final product is as high as 14·5° C., and as it is a well-known fact that the mixture of any oil with 35 per cent. of normal paraffins would have a much higher melting point at this molecular weight, it seems very plausible to assume the presence of *iso*paraffins in the oil under investigation.

On the other hand, as the yield of the hydrogenated oil was only 7·5 per cent., the amount of *iso*paraffins in the investigated Pennsylvanian oil might reach the value of 2·5 to maximum 5 per cent. Such a small percentage of *iso*paraffins may have only a slight effect, if any, on the physical properties of lubricating oils.

As the Pennsylvanian oils are considered to have the most paraffinic character, it is very probable that the other types of oils contain smaller proportions of *iso*paraffins. This supposition is confirmed by the statement of Mair and Willingham,[6] who, investigating the Mid-Continent Crude, found " no evidence whatever for the existence of *iso*- or branched-paraffins in the lubricating oil fractions."

## Summary.

An attempt has been made to isolate the *iso*paraffinic hydrocarbons from lubricating oil fractions. Starting with a material of a paraffinic character, and applying only such methods as cannot result in any destruction of molecules—*i.e.* using only acid treatment, selective extraction and crystallization—the isolation of *iso*paraffins, as well as the quantitative separation of aromatic constituents from the mixture of hydrocarbons, has proved impossible. The final products obtained, corresponding, for instance, to a formula $C_nH_{2n+0\cdot4}$, consist of a mixture of aromatic, naphthenic and paraffinic hydrocarbons, which, being very similar in their physical properties, are no longer separable by means of applied methods.

From very careful analysis of the hydrogenated final product it may be seen, however, that the lubricating oils, especially the light ones, contain some branched paraffinic hydrocarbons. The low melting point—14·5° C. —and the high molecular weight—480—make it probable that the mixture consists partly of *iso*paraffins. Their amount, however, seems to be too small to have any important influence on the physical properties of lubricating oils.

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# THE FORMATION OF ORGANO-METALLIC ALKYL DERIVATIVES OF ALUMINIUM DURING THE POLYMERIZATION OF ETHYLENE.*

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SUMMARY.

The reaction of ethylene under pressure with aluminium chloride has been shown to be fundamentally changed by the presence of metallic aluminium. Under suitable conditions of temperature a high yield of a reactive organo-metallic compound of aluminium is obtained, analogous to the reactive metallic alkyls. The isolation of the liquid compound, which is spontaneously inflammable in air, is described. The properties of the fraction indicate it to be a mixture of the aluminium ethyl chlorides, the existence of which has not previously been reported. By reaction with sodium chloride, formation of a double compound is observed, and the analysis of the residual liquid corresponds closely with that of aluminium diethyl chloride. The catalytic polymerization of ethylene under pressure at 300° C. by the aluminium diethyl chloride fraction has been investigated. The nature of the polymerization products—ethylene homologues of relatively simple constitution—is in accordance with the reaction mechanism proposed by Taylor and Jones for the polymerization of ethylene by free ethyl radicles.

DURING a study of the polymerization of ethylene under pressure by aluminium chloride [1] it was found that in the presence of metallic aluminium the character of the reaction could be altered completely. At temperatures of 100–200° C. the period of activity of the catalyst was relatively short. The product of reaction was a mobile fuming liquid, the characteristics of which recalled those of reactive organo-metallic compounds such as aluminium triethyl, zinc diethyl and the Grignard reagent. This is in marked contrast to the product obtained by the polymerization of ethylene with aluminium chloride alone, which is a hydrocarbon oil together with an insoluble pasty or carbonaceous complex of aluminium chloride and unsaturated hydrocarbons. The polymerization reaction in the presence of metallic aluminium is discussed in another publication. The present paper is concerned with the character of the reactive aluminium compounds formed.

## EXPERIMENTAL.

The polymerizations were carried out in a 2-litre rotary steel autoclave, no liner being used. In a typical experiment the autoclave was charged with 60 gm. of anhydrous (sublimed) powdered aluminium chloride and 20 gm. aluminium powder (grade C.A. 1, British Aluminium Co.), ethylene introduced at 53 atm., the autoclave heated to 150° C. (direct gas heating) and maintained at this temperature for 2 hours.

Final pressure (cold) = 36 atm.
Ethylene absorbed = 17 atm.
Maximum pressure = 95 atm. at 120° C.

* Paper received 14th October, 1937.

50 gm. petroleum ether introduced into autoclave.

| | |
|---|---|
| Total yield (+ solvent) | = 245 gm. |
| Ethylene absorbed | = 115 gm. |
| Weight of centrifuged solution | = 217 gm. |

The variation in the character of the polymerization product with change in conditions is illustrated in the following table, an excess of aluminium being used in each case. The analytical figures were determined by hydrolysis and subsequent estimation of aluminium and chlorine in the aqueous extract. The final column in the table gives the percentage of aluminium present in excess of that corresponding to aluminium chloride.

| Catalyst (gm.). | Reaction temp., ° C. | Reaction time, hrs. | Analysis of Product. | | | % Al excess over $AlCl_3$. |
|---|---|---|---|---|---|---|
| | | | % Al. | % Cl. | Atomic ratio Al : Cl. | |
| 30 $AlCl_3$ : 10 Al (Al granules) . . | 100° | 3·5 | 8·6 | 13·1 | 1 : 1·17 | 5·3 |
| ,, ,, | 180° | 2 | 6·95 | 10·8 | 1 : 1·18 | 4·2 |
| ,, ,, | 300° | 1 | 4·1 | 7·1 | 1 : 1·32 | 2·3 |
| 30 $AlCl_3$ : 10 Al (Al powder) . . | 200° | 1·5 | 12·1 | 22·0 | 1 : 1·38 | 6·5 |

## Qualitative Reactions of the Polymerization Product.

The product from the 100–200° polymerizations was a mobile, clear brown liquid, evolving dense white fumes and becoming heated on exposure to the air. It reacted violently with water, phenol, alcohols and certain chloro compounds (amylene dichloride, benzyl chloride, but not chlorobenzene). When decomposed with water, quantities of an inflammable gas, which was chiefly ethane, were evolved, a viscous hydrocarbon oil was produced, and the aqueous solution contained aluminium and chlorine ions (cf. previous table).

Oxidation of a 25-ml. sample by exposure (in kerosine solution) to dry air over 20 days, with subsequent hydrolysis and distillation, gave 3 ml. of a distillate identified as ethyl alcohol from the boiling point, and melting point of the dinitrobenzoyl ester. A similar sample of the polymerization product was found to react vigorously with acetyl chloride in petroleum ether solution, giving a brown, tar-like deposit. After decomposition of this with ice-cold water, followed by distillation, 3 ml. of a fraction was isolated, identified as methyl ethyl ketone from the boiling point, and melting point of the dinitrophenylhydrazone. These reactions are in agreement with those of such reactive organo-metallic ethyl compounds as aluminium triethyl. It is considered that the product from the ethylene polymerization is a solution of these organo-metallic compounds in a viscous hydrocarbon oil.

## Isolation of an Aluminium Ethyl Derivative.

Preliminary vacuum distillation in a short packed column showed that a reactive liquid of narrow boiling range could be isolated readily from the

crude polymerization product. A typical distillation curve is given in Fig. 1, and shows the well-marked plateau corresponding to the aluminium complex boiling at approximately 85°/10 mm.

308 gm. of a petroleum ether solution of the product obtained by polymerization at 150° C. were distilled from a "Hempel" flask assembly, the neck of the flask being packed to a depth of 15 cm. with 3 mm. aluminium rings.

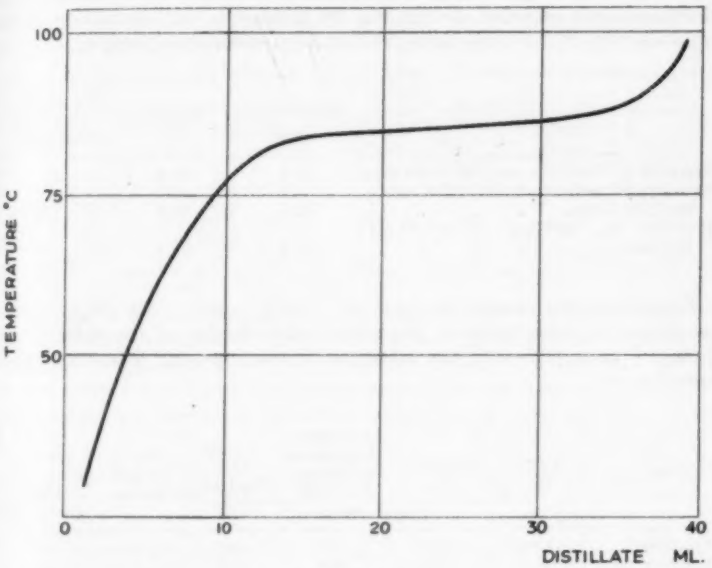


FIG. 1.

DISTILLATION CURVE OF CRUDE POLYMERIZATION PRODUCT CONTAINING THE ORGANO-METALLIC ALUMINIUM COMPOUND. [AT 10 MM.]

A "Bredt" type receiver was used, and the final stages of the distillation were carried out at approximately 10 mm. pressure.

| | | | |
|---|---|---|---|
| Fraction 1. | Petroleum ether and loss . . | 70·5 gm. | 23% |
| Fraction 2. | Below 85·5°/11 mm. . . | 8 gm. | 2·5% |
| Fraction 3. | 85·5°/11 mm.–87·5°/10 mm. . | 106·5 gm. | 34·5% |
| Residue above 87·5°/10 mm. . . . | | 123 gm. | 40% |

The residue was a very viscous brown hydrocarbon oil, containing traces of reactive aluminium compounds. 68 gm. of the main fraction (Fraction 3) were refractionated in a 150-ml. pyrex flask, with fused-on column, packed to a depth of 38 cm. with aluminium wire helices and lagged with asbestos; the following fractions were obtained:

| | | | |
|---|---|---|---|
| Fraction 1*a*. | 64°/10 mm.–85·5°/10·5 mm. . . | 4·6 gm. | 6·8% |
| Fraction 2*a*. | 85·5°/10·5 mm.–86·5°/10·5 mm. . | 41·8 gm. | 61·7% |
| Fraction 3*a*. | Residue + loss . . . . | 21·4 gm. | 31·5% |

In both distillations the initial fractions were yellow in colour, unstable, and consequently discarded. Both of the main fractions (Fraction 3 and Fraction 2*a*) and the residual Fraction 3*a* were clear, colourless liquids which remained unaltered on long exposure to light. They were spontaneously inflammable in air—burning with a luminous, green-edged flame, evolving fumes of hydrogen chloride—and reacted explosively with water.

The volume of gas evolved upon hydrolysis, and the percentage of aluminium and chlorine (determined by hydrolysis and estimation in the aqueous extract) for these three fractions are summarized below:

| | Aluminium, %. | Chlorine, %. | Gas Evolved at N.T.P. ml./gm. |
|---|---|---|---|
| Fraction 3. 85·5°/11 mm.–87·5°/10 mm. | 21·6 | 35·9 | 317 |
| Fraction 2*a*, redistilled 85·5°/10·5 mm.–86·5°/10·5 mm. . . . . | 22·1 | 36·8 | 313 |
| Fraction 3*a*, residual above 86·5°/10·5 mm. . . . . | 21·7 | 33·1 | 329 |

Expressing the results in terms of "$AlCl_3$" and "$Al(C_2H_5)_3$"—as a convenient representation of the relative distribution of the chlorine and "ethyl" groupings with the trivalent aluminium—the following figures were found:

| Fraction. | $AlCl_3$, %. | $Al(C_2H_5)_3$, %. | Calculated Equivalent of Ethane Evolved, ml./gm. | Actual Gas Evolved, ml./gm. | Al : Cl Atomic Ratio. | Total per cent. Al + Cl + ($C_2H_5$) Calculated. |
|---|---|---|---|---|---|---|
| Fraction 3 . | 45·0 | 52·8 | 311 | 317 | 1 : 1·26 | 97·8 |
| Fraction 2*a* . | 46·1 | 54·0 | 318 | 313 | 1 : 1·27 | 100·1 |
| Fraction 3*a* . | 41·5 | 56·1 | 331 | 329 | 1 : 1·16 | 97·6 |

The figures obtained do not approximate to those for any simple compound involving aluminium, chlorine and the ethyl radicle, and the relatively small difference between the composition of the three fractions indicates the need for more effective separation than that given by fractional distillation.

### Separation with Sodium Chloride.

It was found that sodium chloride, at temperatures of the order of 200° C., would react with a portion of the liquid fractions previously described. A liquid lower layer was formed, which solidified on cooling, this interaction indicating the probable formation of a double compound with sodium chloride. With an excess of sodium chloride a residual liquid (an upper layer) was obtained which was inactive towards sodium chloride, and which could be distilled off. The double compound formed was not the simple molecular compound $NaCl,AlCl_3$, for it proved very reactive towards water, evolving quantities of ethane.

A quantitative separation of a portion of the first distillate fraction

(Fraction 3, b.p. 85·5°/11 mm.–87·5°/10 mm.) was carried out, 32·4 gm. being heated with 16·6 gm. of sodium chloride for 40 minutes at 200° with agitation. The upper liquid layer (15·2 gm. = 47 per cent. of original) was separated from the solidified residue (33·2 gm.) and treated with a further 5 gm. of sodium chloride at 200°. No further action was apparent, and the liquid was distilled in vacuum.

The main fraction (b.p. 85–86·5°/9·5 mm., wt. = 11·5 gm. = 35·5 per cent. on initial fraction) gave on analysis: Al 21·7 per cent., Cl 27·9 per cent., gas evolved on hydrolysis 386 ml./gm. Expressing these results in the manner previously adopted, this can be represented as:

| Fraction. | $AlCl_3$, %. | $Al(C_2H_5)_3$, %. | Calculated Equivalent of Ethane Evolved, ml./gm. | Actual Gas Evolved, ml./gm. | Al : Cl Atomic Ratio. | Total per cent. Al + Cl + ($C_2H_5$) Calculated. |
|---|---|---|---|---|---|---|
| Original Fraction 3 . | 45·0 | 52·8 | 311 | 317 | 1 : 1·26 | 97·8 |
| After NaCl treatment . | 35·0 | 61·8 | 364 | 386 | 1 : 0·975 | 96·8 |

The figures for the final fraction approximate fairly closely to those for the compound aluminium diethyl chloride—$Al(C_2H_5)_2Cl$, alternatively $AlCl_3,2Al(C_2H_5)_3$—having an Al : Cl atomic ratio of 1 : 1·00, as may also be seen from the comparable aluminium and chlorine figures given below:

| | Aluminium, %. | Chlorine, %. |
|---|---|---|
| Composition of compound $Al(C_2H_5)_2Cl$ . . . | 22·4 | 29·4 |
| " " " for 96·8% concentration . . . . . | 21·7 | 28·5 |
| Composition of fraction analysed . . . | 21·7 | 27·9 |

The final fraction had a b.p. at 750 mm. of *circa* 214–215° C. (cf. $Al(C_2H_5)_3$, b.p. 194°; $AlCl_3$, b.p. 183°); it gave no sign of solidification at −70° C.

Analyses were carried out on the gas evolved upon hydrolysis of this fraction, and also on the gas from a sample of zinc diethyl (B.D.H.). The figures obtained, using the Bone and Wheeler apparatus, are given below:

| | Gas from Hydrolysis of | |
|---|---|---|
| | " Aluminium Diethyl Chloride," %. | Zinc Diethyl, %. |
| Higher olefines . . | 0·1 | 0·7 |
| Ethylene . . . | 5·5 | 5·5 |
| Oxygen . . . | 0·9 | 0·5 |
| Hydrogen . . . | 4·7 | 0·4 |
| Paraffins * . . . | 86·8 | 90·8 |
| Nitrogen . . . | 2·0 | 2·1 |
| Value of " n " . . | 2·00 | 1·98 |

* By combustion over copper oxide.

The oxygen and nitrogen are attributable to traces of air contaminating the hydrolysis apparatus. The presence of ethylene and hydrogen is not in agreement with the general view that hydrolysis of the simpler reactive metallic alkyls gives rise solely to the corresponding paraffin. The gas from the zinc ethyl likewise contained a similar quantity of ethylene, but practically no hydrogen; the purity of the sample of zinc ethyl used was not, however, established.

Grignard and Jenkins [3] stated that the ethyl aluminium iodides gave pure ethane in quantitative yield on decomposition with water, but no analyses were reported. The presence of hydrogen and olefines in the hydrolysis products of crude alkylated derivatives of aluminium and magnesium, reported by Spencer and Wallace,[4] is attributable to impurities. In the present instance, the approximate equivalence of the hydrogen and ethylene almost suggest a hydrolytic equivalent to the well-known thermal decomposition of magnesium ethyl.

$$Mg(C_2H_5)_2 = MgH_2 + 2C_2H_4.$$

Apart from the presence of these unexplained components, the main product of hydrolysis—ethane—is in agreement with that expected from the decomposition of aluminium triethyl or its halogen derivatives.

### Sodium Chloride Double Compound.

The double compound, separating on treatment of the original fraction with sodium chloride, was not homogeneous, owing to segregation of excess sodium chloride, and was reactive to air. Duplicate analyses are summarised below:

| | 1. % | 2. % |
|---|---|---|
| Total chlorine (as chloride) | 54·4 | 55·0 |
| Aluminium | 9·4 | 8·1 |
| Sodium chloride | 56·4 | 62·4 |
| Gas evolved, ml./gm. | 90 | 79 |

From these results the following figures have been calculated:

| | % | % |
|---|---|---|
| Sodium chloride | 56·4 | 62·4 |
| Aluminium chloride | 25·3 | 21·4 |
| Aluminium triethyl | 18·1 | 15·8 |
| | 99·8 | 99·6 |
| Calculated volume of ethane ml./gm. | 106 | 93 |
| Al : Cl atomic ratio (for the $AlCl_3$ + $Al(C_2H_5)_3$) | 1 : 1·63 | 1 : 1·61 |

Since the residual liquid from the treatment with sodium chloride is considered to be aluminium diethyl chloride, and is inactive towards that salt, it is probable that the solid complex investigated is largely a double compound of sodium chloride with *aluminium ethyl dichloride*, together with aluminium diethyl chloride in admixture or in solid solution.

### Catalytic Polymerization of Ethylene.

In view of its relation to the constitution of these compounds, the catalytic polymerization of ethylene by the final "aluminium diethyl

chloride " fraction has been investigated and is briefly summarized here. Using a 2-litre rotating steel autoclave, with 43·5 gm. of the " aluminium diethyl chloride " (obtained by sodium chloride treatment), and ethylene to an initial pressure of 48 atm., no pressure drop was observed up to 200° C. At 250° C. the pressure fell at the rate of 0·44 atm./min., increasing to 2·0 atm./min. at 300° C. Continuing the polymerization at 300° C., a total yield of liquid polymers of 422 gm. was obtained. After washing with alkali and water, 74·6 per cent. of the product distilled below 200° C. The 30–100° and 100–200° fractions had (addition) bromine

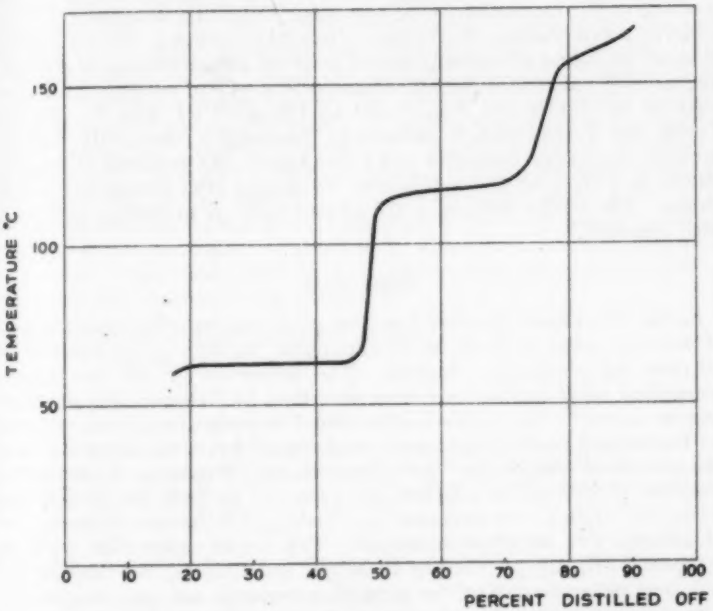


FIG. 2.

DISTILLATION CURVE OF HYDROCARBON PRODUCT FROM THE POLYMERIZATION OF ETHYLENE AT 300°C. WITH " ALUMINIUM DIETHYL CHLORIDE " CATALYST.

numbers of 165 and 105, respectively, indicating a high degree of unsaturation (80–100 per cent.). Approximately 15 per cent. of low-boiling olefine polymers were present, considered to be butene-1 from the boiling point (−6° C. on the Podbielniak distillation apparatus) and formation of the dibromide (b.p. 162–164° C., cf. 166° given in Beilstein). The distillation curve (using a 50-cm. vacuum-jacketed Dufton column) on the remainder of the fraction below 200° is reproduced in Fig. 2, the boiling points being uncorrected. Comparable data were obtained when using a catalyst composed of 15 gm. $AlCl_3$ + 15 gm. aluminium powder. From these results it is concluded that the major portion of the polymerization product is composed of ethylene homologues of even carbon atom groupings, *i.e.* butene,

hexene, octene, etc., with a remarkable absence of isomers or odd carbon atom polymers (from the sharpness of the distillation plateau). Similar results were obtained for polymerisation with the crude "aluminium ethyl chloride" fraction, but the product was more saturated, contained a much higher proportion of high-boiling polymers, and gave a less clearly defined distillation curve.

The data from the polymerization of ethylene by the "aluminium diethyl chloride" are particularly interesting. The temperature of initial polymerization (*circa* 250°) is closely similar to that found by Roux and Louise [8] for the incipient decomposition of aluminium triethyl. The products of polymerization are in agreement with those anticipated for the catalytic polymerization of ethylene by free ethyl radicles. The production of small quantities of olefine polymers from the polymerization of ethylene by free ethyl radicles (by thermal decomposition of lead tetraethyl) has been reported by Taylor and Jones [9] and by Cramer [10] (cf. Rice [11]). By the Taylor and Jones reaction mechanism, involving a three-body collision between two olefine molecules and a free radicle, the products of reaction should be a range of olefine polymers, containing even numbers of carbon atoms. The results obtained in the present work are in striking agreement with this view.

## Discussion.

So far as is known, no work has been published reporting the formation of reactive ethyl derivatives of aluminium through polymerization of ethylene by aluminium chloride. The properties of the two known aluminium ethyl iodides have been described by Grignard and Jenkins [3] and by Leone.[2] The corresponding mixed bromides have been prepared by Furstenhoff [5] and by Grignard and Jenkins,[3] but with no separation of the individual compounds. An organo-metallic derivative of aluminium, assumed to contain an ethylene grouping and to have the constitution $AlBr_3,Al(C_2H_4Br)_3$, was prepared by Furstenhoff [5] through interaction of aluminium with ethylene dibromide. This seems comparable with the compound $CH_2{:}AlI$, prepared by Faillebin [6] and Thomas,[7] but the constitution and elementary character of these compounds are open to question. The aluminium ethyl chlorides have not, apparently, been prepared.

The reactions and analytical data described in the experimental part support the view that the compounds described are aluminium ethyl chlorides.

No comparable reaction between sodium chloride and aluminium ethyl halides appears to have been reported. In view, however, of the ease of formation of the aluminium chloride–sodium chloride molecular compound, it appears not unreasonable for aluminium ethyl dichloride to form an analogous complex, and for the diethyl chloride to be inactive. It would be anticipated that the reactions of the ethyl chlorides would lie between those of aluminium chloride and aluminium triethyl. From the properties of the first crude reactive fraction obtained, particularly the absence of any polymerizing action on ethylene at temperatures up to 200° C., it seems most improbable that there is any aluminium chloride present in this fraction. It is considered that:

(1) The original crude fraction is a mixture of aluminium ethyl dichloride

and aluminium diethyl chloride, with possibly a trace of aluminium triethyl.

(2) With sodium chloride the aluminium ethyl dichloride forms a double compound, containing a proportion of the diethyl chloride as a solid solution.

(3) The residual fraction, inactive towards sodium chloride, is essentially aluminium diethyl chloride, with possibly a small proportion of aluminium triethyl.

The mechanism of the reaction by which these ethyl derivatives of aluminium are formed is not known. The polymerized hydrocarbons formed during the reaction have a hydrogen deficiency (as determined by micro-combustion analysis) more than sufficient to account for the production of the ($C_2H_5$) groupings from the initial ($C_2H_4$) molecules. It is probable that these are formed by intermolecular hydrogenation of an unstable transient complex between the ethylene and aluminium chloride, in the presence of metallic aluminium, by hydrogen liberated at the expense of the polymerized hydrocarbons formed. Intermolecular hydrogenation of this nature [12] is known to be characteristic of many reactions involving aluminium chloride and similar catalysts at elevated temperatures. It is significant that the present reaction proceeds at temperatures at which, in the normal polymerization of ethylene by aluminium chloride, quantities of paraffin hydrocarbons are formed—a reaction attributed by Ipatieff [12] to this type of intermolecular hydrogenation.

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# THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

## Nineteenth Annual Dinner.

The Nineteenth Annual Dinner of the Institution was held at the Connaught Rooms, London, on Friday, 8th October, 1937. In the unavoidable absence of the President, Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc., the Chair was taken by Sir Thomas H. Holland, K.C.S.I., K.C.I.E., F.R.S., Hon.LL.D. Nearly two hundred members and guests were present, including the following :

Sir Henry T. Tizard, K.C.B., Colonel L. Pineau, Prof. L. Ubbelohde, J. H. C. De Brey, Maj.-Gen. S. C. Peck, C.B.E., J. B. Aug. Kessler, Sir John Thorneycroft, K.B.E., Sir George Lee, O.B.E., W. A. S. Calder, F. C. Starling, S. Scheer, J. Filhol and E. S. Shrapnell-Smith.

## Messages.

The Loyal Toast having been honoured, the Chairman said : We have received one or two messages to which I should like to refer. The first is from our President, Colonel Auld, and is addressed to me by name :—

> " Greatly regret my inability to be with you to-night. Please accept my best thanks for taking the Chair and convey my greetings to Sir Henry Tizard and all guests, particularly Colonel Pineau, Professor Ubbelohde and Mr. De Brey. Best wishes for a successful evening."

I propose, if you approve, to reply :—

> " I have received your kind message, which is greatly appreciated. The others missed you."

(Laughter and applause.)

I also have a message from the Trinidad Branch, conveying greetings to the parent Institution, and I propose, with your approval, to send a similar message of greeting back to Trinidad and to the other branches abroad. We have four branches abroad and two at home, and, if you approve, I will send a message to all of them. (Applause.)

In the absence of the President, I am sure you will appreciate how grateful I feel at having to preside at a dinner, after so many in Scotland, where it is inappropriate, and even impertinent, to sing " Auld Lang Syne ! " (Laughter.)

## " The Institution of Petroleum Technologists."

Sir Henry T. Tizard, K.C.B., M.A., F.R.S., who proposed the toast of the Institution, said : It is, of course, a great honour, and in most ways a great pleasure, to me to be called upon to propose this toast, because

[*Fradelle and Young.*

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS NINETEENTH ANNUAL DINNER, 8TH OCTOBER, 1937.

*Standing* (*left to right*): W. A. S. Calder, Sir George Lee, O.B.E., M.C., E. S. Shrapnell-Smith, C.B.E., F. C. Starling, Sir John Thorneycroft, K.B.E., Prof. A. W. Nash, Sir Henry T. Tizard, K.C.B., Sir Thomas Holland, K.C.S.I., K.C.I.E. (Chairman), Col. L. Pineau, J. B. Aug. Kessler, Prof. Dr. L. Ubbelohde, J. H. C. De Brey, S. Scheer, Maj.-Gen. S. C. Peck, C.B.E., D.S.O., Eng-Capt. G. C. P. Burt.

[*To face p.* 688.

UNIV. OF MICH.

I know a good deal about the work of the Institution, and I think I can say that I have a good many friends among its members. But of course this is essentially the kind of speech which is very much better in the taxi going home than in the taxi coming to the dinner, and is worst of all at the dinner itself. (Laughter.) However, those of you who have been in a similar position to me will, I am sure, sympathize with me, and those of you who have not will offer me your goodwill.

I think that it is right for me to offer congratulations to the Institution, and that you can feel that you have earned any praise that a speaker can give you; because, after all, it is something to be proud of that in this country, where we have no natural reservoirs of oil—at least, not at present (laughter)—this Institution has attained a prominent if not a commanding position in the field of petroleum technology.

There is no need for me to tell you of the advances in the science of petroleum since the beginning of this century, but they are certainly of the utmost interest. I do not need to tell you of how petroleum technology has grown from pure empiricism to the exact application of science to all its branches. (*A member laughed.*) Well, I am glad that somebody questioned it! I thought it was only right for a scientist to pretend that it was so. (Laughter.) I can at any rate say with truth that, whatever the demands of the consumer, they have in fact been met up to now, and that they have been met is largely due to the technologists.

I do not pretend to a very close knowledge of the history of the subject, but I have been connected during the last two years with an enterprise of which many of you know—namely the production of a work called *The Science of Petroleum*. I have taken a very minor part in this, but I am glad to have my name associated with it; it is always nice to have one's name associated with something good which one did little to help. (Laughter.) It gives me the opportunity of saying that I am proud to think that that work, which will be issued shortly, has originated in Great Britain on the initiative of two of your members, is connected in a very important manner with my old University, has been helped very largely by my new University, and is being brought out with the help and collaboration of all the important people in the whole world of petroleum technology, including in particular the most important of your foreign colleagues. I mention it, too, because it gives me the opportunity of saying that if the work is the success and the benefit to you that we hope, it will be largely due to my friend Professor Nash, who is here this evening, and to his colleagues in Birmingham. (Applause.)

I have said that I need not tell you of the advance of petroleum technology, about which you know more than I do; but I wonder whether it has ever occurred to you that we are witnessing to-day a kind of industrial revolution which is just as important and just as interesting as the Industrial Revolution of the nineteenth century. In the nineteenth century, after the Napoleonic Wars, it was said that England was left a crippling debt which was never discharged but, by the exploitation of coal, was rendered negligible. In the same way, the last War has left us with a crippling debt, which perhaps also will never be discharged, but which in the course of time will be rendered negligible by the direct and indirect results of the exploitation of oil. Comparisons between the present time

and a hundred years ago are extremely interesting. The similarities are interesting and the differences are interesting. A hundred years ago the Industrial Revolution was on its way with the exploitation of coal. Road transport was being knocked out by the railways. To-day road transport is not knocking out the railways, but improving them. In those days the industrial revolution based on coal led, I think it would be right to say, to the wealth of the few and the squalor of the many; in these days the industrial revolution which is based on the exploitation of oil has brought real wealth, possessions, occupation and happiness to millions of people. (Applause.) In those days—you can see the relics of it as you go round the country—the change led to squalid houses, horrible districts, scars on the face of the country; now, if you go about the country you will find new public-houses on the roads (laughter) which are not at all unpleasing in their elevation, and offer refreshment to the far from weary traveller. (Laughter.)

We shall all admit, of course, that the exploitation of oil, great though its direct and indirect advantages have been to the whole world, has brought with it its disadvantages. One of the most remarkable of its disadvantages is the entire disappearance of the extraordinary capacity for repartee of the old horse-cab driver. (Laughter.) There are, of course, other disadvantages. (Laughter.) Some of those disadvantages are brought very closely to our notice nowadays, and many serious people in the country doubt whether this country is not going to suffer more than it gains by the exploitation of oil. I am not one of those who believe that the prosperity of any country is really going to depend in future mainly on its natural resources. I think that that time has passed, and that the prosperity of any country will depend mainly on the skill and the brains and the adventure of its people. (Cheers.) But there is no denying that there are serious national problems connected with the widespread use of imported oil.

My feeling about such problems is this. Every scientific man and every technologist should endeavour to give the very best unbiased advice he can, and no scientific man, however expert he is at his own subject, should pretend to be able to pronounce with confidence on problems of economic and national importance. It is his duty to give his advice and views without fear, so that those who have to decide these matters can feel that they have the best information available. I must say that it is sometimes difficult. I once myself gave vent to opinions—based, I thought, on scientific reasoning—on the value of the production of oil from coal in this country, and on the possibility that the optimistic views which were taken of it were not very well founded, and I got into trouble at once. I think the right expression would be that I was hauled over the coals! (Laughter.) I remember that one gentleman pushed his censure so far as to refer to me in the public press as a professor (laughter), and he even spoke of me, in a moment of extreme sarcasm, as a learned professor. (Laughter.) On the whole, I think that those views have been fairly well founded; but I do say this—that, having given to the best of our ability—and you, I think, are in a position to do so—our views on matters of national importance connected with the use of oil or coal, we should be content that the final decision has to be taken by other people; and, when that decision is

taken, whether we agree with it or not, you will agree with me that it is our duty to try to make a success of it, even if it involves digging large holes in the ground for fun. (Loud laughter.) After all, if any technical experiment is carried out even on a large scale with technical skill and imagination, what does it matter if it is not a complete success? I can imagine many worse ways of spending national money than that! (Laughter.)

I am going to take this opportunity of mentioning one thing which sometimes troubles me at the Imperial College. One specific task laid down in our charter is that of educating men in the highest branches of science and technology; it is our duty to educate those whom even you, and certainly the outside world, would call specialists. Now, the specialist is very often derided by people who are not specialists. They regard his lack of general information as something occasionally to be laughed at; but is it not true to say that almost all the major advances in science and industry are made by specialists? There are certain branches of learning nowadays—and you, I am sure, could think of some connected with your own industry—where it is of extreme importance to educate extreme specialists, but where very few of them are needed. The future of industry depends so much, directly and indirectly, upon such men that it does cause me some anxiety to observe that they often have a very insecure career, for reasons over which they have no control. All the industries of the country, including your own, have to find a way of solving that difficulty somehow, and you who represent petroleum technology can, I feel, bring a powerful influence to bear. I do not know whether you remember Kipling's lines about Tommy:

> 'O! it's Tommy this, an' Tommy that, an' "Tommy, fall behind";
> But it's "Please to walk in front, sir" when there's trouble in the wind.'

The specialist in industry is often in that position.

I want, in conclusion, to say how sorry I am that your President is not here to-day. I have to couple this toast with the name of Sir Thomas Holland. (Applause.) I do not think it would be proper for me to offer him any compliments, so I will merely say that it often grieves me very much to observe how much he is missed at the Imperial College (laughter), of which he is one of the most distinguished sons. (Applause.) I ask you to drink to the health of the Institution, coupled with the name of Sir Thomas Holland. (Applause.)

The Toast was enthusiastically received.

The Chairman (Sir Thomas H. Holland, K.C.S.I., K.C.I.E., F.R.S., Hon.LL.D.), who responded, said: I appreciate very much the honour which Colonel Auld has conferred on me in asking me to occupy—he knew quite well that I could not adequately fill—his place. In his absence, he has selected one of the old Past Presidents, who has been on the shelf for a good many years, now taken down and dusted for temporary work. (Laughter.) My absence recently has not been entirely my own fault; living in Edinburgh, one feels very much the fact that this Institution, having been founded in London, is situated so far from the recognized

centre of culture of these islands. (Laughter.) Nevertheless, it is true that I am not as fitted as I know some of the other Past Presidents are to undertake this task, because I am expected to speak of the current activities of the Institution. But, after all, coming back to old friends is very good for one. It makes one realize the years that are passing to find that one is among the nine original founders of this Institution surviving out of the twenty-nine who were living when the inaugural meeting was held in London on 3rd March, 1914.

Sir Henry Tizard has touched on a point which is extremely interesting to those of us who are responsible in the matter in regard to science, and especially its borderland of technology—namely, what should be the kind of training given to the man who is to take up more than what we call one specialized science in a University? I would recall to you how the idea of this Institution arose. We had a Royal Commission on the introduction of oil fuel into the Navy, with Lord Fisher as Chairman and Lord Jellicoe, Sir Boverton Redwood (our founder), and Sir George Beilby among the members. At lunch time in the Athenæum, of all places, one day we realized that our witnesses were showing that chemistry and engineering and geology were in some way so related to one another in their application to oil that surely the three could be brought together into a compact body. Probably I was the most refractory amongst those who discussed the question, having been brought up to think that chemistry was chemistry and geology was geology. We realized, however, that our witnesses had a common object, and that, just as the student of medicine applied particular sciences to his education, so, too, we might do the same for the development of oil; and out of that idea arose the idea of a Petroleum Technologist and this Institution.

I do not think that anyone, knowing the history of the Institution, would think for a moment that I was correct in doubting that Sir Boverton Redwood was right in formulating this notion. That was about 1912 and 1913; but in 1912 we were practically anticipated by work which was being done at Birmingham, where Professor John Cadman started a course in what was then known in the Birmingham University as petroleum mining. Cadman was a pioneer at that time; he started two years ahead of the Imperial College. Since then—and this is further evidence of the breadth of his imagination—Professor Cadman, later as Sir John Cadman and now as Lord Cadman, has extended the same bright thought to the whole commercial aspect of oil, and has brought together the great companies in the world which were formerly at war with one another now to realize that they can help one another to one another's good. (Cheers.) It is because of his genius and his generous recognition of the rights of other people that these companies have now begun to exchange thoughts with one another. I think that the latest, and I am sure you and I agree not the last, of the honours conferred upon him has been most popular in this Institution, as well as in the oil world at large. (Applause.)

We started in 1914 with 146 members, and we have now grown to 1,440 members. (Applause.) The Institution has devoted some of its funds to research, and has helped in giving scholarships at Birmingham and South Kensington to encourage students who are coming on. But

the *Journal*, I think, has been the greatest success among the products of the Institution, and for that we have to thank first Dr. Dunstan for the irrepressible energy which he has shown, not only in working himself, but in inspiring others to do their share. (Applause.) I am sure you will agree with me that Dr. Dunstan would like that recognition of his great work to be passed on to those who have been his willing colleagues, and especially to George Sell. (Applause.) We wish Mr. Sell, who has been a member of this Institution for seventeen years, from student to full member, and who has been in many other ways our helper, great success in his new sphere. (Applause.) At the same time, we welcome to succeed him Miss Tripp, who promises us further success. (Applause.)

I have already mentioned our Branches, to whom we have agreed that a message of goodwill should be sent. These branches have arisen not by the direct activity of the Council, but by spontaneous local growth. The members of our Institution are, naturally, largely abroad. We therefore greatly appreciate the work that has been done by the formation of these local branches, and the Council has willingly and readily supported the work which has been done, especially in these four or five centres overseas.

I should like to mention that the World Congress which was held four years ago in London, and this year in Paris, has resulted in the formation of a permanent Bureau to carry on Congresses of this kind in future. We are glad to welcome to-night the President of the Bureau, Colonel Pineau, and his colleagues. (Applause.) But I must leave further remarks on this point to Professor Nash, who is to follow.

I would also ask you to take note of the fact that we are to have in Scotland a conference on shales and cannels organized on behalf of this Institution. Capt. W. H. Cadman has been to Edinburgh and then on to Glasgow—the proper order!—and, through his remarkable enthusiasm and keenness, he seems to have gathered together all the people who matter in the South of Scotland to support this conference, which is to take place next June. He has been roping in members of the Government one by one, and Lord Elgin, the Chairman of the great Empire Exhibition to be held in Glasgow throughout the summer, and so we look on this conference as one of the features which will give that great Empire Exhibition some justification. (Laughter.) I invite those of you who are not too far from the centre of culture to come to Scotland and take part in the conference.

I thank Sir Henry Tizard very cordially for his delightful speech, and the members of the Institution and our guests for responding generously to the Toast. (Applause.)

## "The Guests."

Professor A. W. Nash (Vice-President), who proposed the toast of the Guests, said: When one is honoured by being asked to propose an important toast such as this, one invariably flies to *Who's Who*, to see what each person concerned has written about himself, or perhaps I had better say to see what each person has allowed to come to light regarding his

past. (Laughter.) On this occasion, however, I am spared this research, because I have the honour of knowing most of our official guests personally; and I would assure them that I shall be perfectly discreet. (Laughter.) It gives me particular pleasure to bid them all a hearty welcome. In doing so, I do not forget that we have with us also the private guests of members, friends who are just as much our guests, and, on behalf of the President and members of the Institution of Petroleum Technologists, I give them an equal welcome.

There is a great deal which could be said about the distinguished guests whom we have with us to-night if time allowed, but I must content myself with a brief reference to each gentleman present. Our guests fall more or less into three categories. First of all, we have the representatives of similar organizations in the world of petroleum science, as exemplified by members of the Congress Bureau; secondly, we have the representatives of industry; and thirdly, the representatives of other technical institutions in London. Sir Henry Tizard and Mr. Starling do not fall exactly into any of these categories, but their sympathies and interests are sufficiently wide to embrace them all.

M. Scheer, as President of our sister institution, the French Institution of Petroleum Technologists, we are particularly glad to welcome to-night. (Applause.) If I do not say more about him, it is because his work and the work of his Institution are so well known to you that any words of mine would be superfluous. Unfortunately, M. Bihoreau, who was to have sat next to me, who is a Past President of the French Institution of Petroleum Technologists and Chairman of the Organizing Committee of the Second World Petroleum Congress, has been unable to arrive. Had he been here, I should have liked to congratulate him on the excellent work which he has done as Chairman of that Committee. (Cheers.) M. Filhol is the indefatigable Secretary of the French Institution of Petroleum Technologists, and was also General Secretary of the Second World Petroleum Congress. We should like to offer him our congratulations on the honour recently bestowed upon him by the French Government. (Applause.)

We are also glad to see with us Mr. Shrapnell-Smith, the Chairman of the Petroleum Industry Committee of the British Standards Institution. (Applause.) There is another gentleman whom I see here to-night to whom I must refer briefly, and that is Mr. Marcus S. Abrahams. (Applause.) Mr. Abrahams was the first General Manager of Balikh Papan as far back as 1895.

As I mentioned at the commencement, it is a difficult task to pay homage adequately to everyone in such a short space of time, and I wish that I could adopt the method used by B.B.C. announcers in the children's hour, so that I could say "Good evening, Sir Henry Tizard. We hope you are enjoying yourself. If you will look behind the piano, you will find a nice new aero engine to play with." (Laughter.) I am afraid, however, that that will not suffice. I am particularly glad to see Sir Henry Tizard here to-night for two reasons. In the first place, I believe that this is the first occasion on which he has attended a dinner of the Institution, and secondly, it gives me the opportunity of expressing in public the gratitude which Dr. Dunstan and I feel for the very able manner

in which he has acted as advisory editor to *The Science of Petroleum*, of which Dr. Dunstan and I are joint editors. Bearing in mind that, apart from his duties as Rector of the Imperial College of Science and Technology, he is also Chairman of the Aeronautical Research Committee, as well as on the Scientific Advisory Board of the Committee of Imperial Defence, and therefore responsible for the scientific aspects of the safety of the British Empire, I marvel that he has had the time to help us in the way which he has. (Applause.) If I may break off at this point to mention another matter, Sir Henry referred in very flattering terms to the work which my colleagues in Birmingham have done in regard to this great work. I should not like this opportunity to pass without expressing to Professor Illing and his colleagues my most grateful thanks for the vast amount of work which they have done, particularly in the geological section.

To Mr. Kessler, still in my capacity of B.B.C. announcer, I would say how much we welcome him, and if he will look in the top drawer of his desk he will find a nice new economic plan, which will explain to the world at large why the big oil companies are such philanthropists. (Laughter.) To be serious once again, Mr. J. B. A. Kessler, who was the originator of the well-known Kessler plan, is known throughout the industry as a well-informed student of economics, and throughout the world as a knowledgeable director of the Shell-Royal Dutch group of oil companies.

We are also grateful to the Presidents of the various Institutions represented here for honouring us with their presence. I always feel very sympathetic towards the Presidents of societies who have to attend functions of this kind, and I think that it would be rather a good idea if all technical institutions had two Presidents, as large ocean liners have two captains, one the executive officer and the other for the more social side of the duties. (Laughter.) The senior President, who would, of course, be a man of mature years, could then be left to direct and control the policy of his society, while the younger President could wade through an eight-course dinner—*and* the wine list—as I could, up to ten years ago, without any regrets the next morning. (Laughter.) We have with us Sir John Thorneycroft, President of the Institution of Mechanical Engineers. (Applause.) As one interested in lubrication problems, I should like to express my appreciation of the efficient manner in which that Institution has organized the forthcoming symposium on lubrication. To Sir George Lee, President of the Institution of Electrical Engineers, we owe a debt of gratitude for the great part which he has taken in the development of trans-continental and trans-oceanic telephony. We are very delighted to have with us also Major-General S. C. Peck, President of the Institution of Automobile Engineers, a body with which we have much in common, and Mr. W. A. S. Calder, Chairman of the Council of the Society of Chemical Industry and Past President of the Institution of Chemical Engineers. (Applause.) Major-General Peck was one of the first holders of a University degree to be appointed directly to a regular commission in the Army. In a lifetime of meritorious service he has many things to his credit, of which I have time to mention only three. In 1920 he was President of the Inter-Allied Commission which carried through the first successful plebiscite

in the world's history, in Southern Austria. Later he was appointed Director of Artillery, in which position he was responsible for the administration of the Research Departments of the Arsenal and of the Military College of Science at Woolwich. Since then he has been Director of Mechanization and responsible for the origin of the Mechanization Board which produced the first real liaison between the Army and the learned engineering institutions. Mr. Calder is known to all chemical engineers as a man who has combined science and industrial art most successfully, realizing the true import of each in an organization the primary function of which is to earn dividends. He is, as you know, Chairman of the Control Committee of the Midland and South Wales Division of the General Chemical Group of Imperial Chemical Industries, and the wonderful success and high standard reached by the Institution of Chemical Engineers are largely due to his efforts. (Applause.)

Then we have with us Mr. F. C. Starling, Director of the Petroleum Department. (Applause.) I am not one who believes that the best legislation must necessarily emanate from our politicians. (Laughter.) I have a greater regard for our civil servants, in that respect, and that is the tribute which I would pay to Mr. Starling.

I now come to three gentlemen whom I have left until last because I wish to couple their names with this toast: I refer to Colonel Pineau, Professor Ubbelohde and Mr. De Brey. (Applause.) Colonel Pineau, who is Director of the Petroleum Department in France under the Minister of the Interior, was *President d'Honneur* of the Second World Petroleum Congress, and is Chairman of the Bureau which is charged with the permanent organization of that Congress. The Second World Petroleum Congress was attended by 1,500 delegates, and I wish to pay, through him, a special tribute to the organizers for the magnificent manner in which they arranged the hospitality for their guests last June. Professor Ubbelohde, who is the head of the Government research organization dealing with mineral oils in Germany, needs no introduction to any body of oil men. His pioneering work in petroleum research, especially upon viscosity and testing methods, is known to everyone. (Applause.) Like most true men of science, Professor Ubbelohde does not advertise himself, and we have to judge him not on what he has said of himself, but on what he has done; and every petroleum technologist throughout the world will agree with me when I say that we have judged him and not found him wanting in this respect. (Applause.) The name of De Brey is known to all refinery men throughout the world, not only as chief technical adviser to the Royal Dutch group, but also as a pioneer in gasoline stabilization and in the recovery of natural gasoline. Mr. De Brey is the President of the Petroleum Section of the Royal Dutch Institute of Engineers. It was he who, together with Professor Waterman, arranged the very successful visit which our members paid to Holland last year, and it is a great pleasure to us to be able to acknowledge in London the help which we received from Mr. De Brey eighteen months ago. (Applause.)

As I have already indicated, I have not been able, owing to the short time at my disposal, to say nearly as much about our guests as I could have wished, and so I would ask you to make up for any remissness on my part by toasting the guests most heartily, and with the toast I couple the

names of Colonel Pineau, Professor Ubbelohde and Mr. De Brey. (Applause.)

The Toast was duly accorded.

Colonel LOUIS PINEAU, who was received with applause on rising to respond, said : My duty, of course, is, on behalf of your fortunate and happy guests, to say "Thank you" most cordially for your very enjoyable entertainment to-night. I must also return thanks for those whom you have so kindly congratulated on their work in the organization of the recent World Petroleum Congress. And now, remembering the custom most happily established by those of your members who have honoured us with their presence at our various festivities in France and favoured us with a speech, I will ask you to allow me to go back to my mother tongue and speak to you in French, being assured that by doing so I shall be much better understood than if I continue to use the English language, with which I am far from being thoroughly familiar. (Applause.)

*Continuing in French, Colonel Pineau said :* If it is true, as was freely stated last year in certain organs of the petroleum press in this country, that there are too many congresses, international and other, occupying themselves with the same questions, it is not less true that a congress to which the technologists of the entire world bring their able assistance presents immeasurable advantages from the point of view of the advance of science and the progress of industry. Taking, for example, the Second World Petroleum Congress of June last, in which so many of you took part, you will have been able, like myself, to observe with what close attention and interest the work of each of the different sections was followed, at which papers were given by some of the most well-known specialists in the world, followed by interesting discussions. I should like to mention in particular the communications dealing with Drilling Muds, Gas Polymerization and Hydrogenation. The lecture theatre was insufficient to hold all those who desired to attend and who were interested in the questions, and the enormous success of the Congress surpassed by far anything for which the Organizing Committee could have hoped, and showed what remarkable results can be obtained by united effort. There is no need for me to tell you how pleased the French Institution of Petroleum Technologists, the energetic President of which, M. Scheer, is with us to-day, was at the success of the Congress and the goodwill shown in making the preparations for it. I would also emphasize the very important part played by the collaboration of your great Institution, whose representatives on the Organizing Committee Mr. Kewley, Dr. Dunstan and Mr. Astbury gave us in all circumstances their most valued help. (Applause.) Moreover, I would say that the energy and faith of the organizers in France made for the success of the gathering. The magnificent success which you achieved in London in 1933 justified such efforts on our part. We are all the more happy to have succeeded in that the Second World Petroleum Congress rendered it possible to take a new step forward in bringing about the collaboration which we have for so long desired between the petroleum technologists of all countries and the great associations to which they belong. The presence at this dinner this evening of representatives of several of those associations who have come here partly to take part in the first meeting

of the Permanent Council of the World Petroleum Congress shows that the putting into practice of the resolutions adopted at Paris is to be actively carried out.

There is one thing which struck me with regard to the very interesting Exhibition of Corrosion held on the occasion of the Paris Congress, and which was due to the initiative and good work of our colleagues of the Royal Dutch Group. As an introduction to this Exhibition the organizers showed that the metals used by man are found in nature in the condition of oxides, sulphates and carbonates, and it is only the work of man which has rendered them utilizable, while the tendency of the metals so produced was to revert to their original state as soon as man abandoned them. That explained what was found as a result of the combined action of air and water and of the various substances which are found, for example, in abundance in the fogs of London. (Laughter.) Only the work of man can attempt to alter that innate tendency of nature. I see in this phenomenon a picture of what should be the character, unceasing and permanent, of human work, and a lesson in how we should follow up what we initiate. It does not suffice to achieve success in a Congress or any other effort, if that success is not followed up. The successful collaboration of the petroleum technologists of the entire world, of which we have seen such a magnificent demonstration, will be forgotten, dispersed and therefore useless if we do not continue to enlarge the good work which has been begun. That is the meaning of the initiative so efficiently taken by the Institution of Petroleum Technologists through one of its Past Presidents, Mr. Dewhurst, which has led to the creation of the Permanent Council of the World Petroleum Congress. (Applause.) The unceasing evolution of our industry, and the magnificent progress which gives us such solid reasons for confidence in its greatness and development, seem to me to make it more than ever necessary to encourage the bringing together of the technologists of all countries for the free interchange of ideas of which we have already seen the fruitful results. I have no doubt whatever that you are all agreed on that, and I give you the assurance that the petroleum technologists of France will in all circumstances remain attached to that collaboration. (Prolonged applause.)

Prof. Dr. L. Ubbelohde, who also responded, said: Lord Cadman at Paris delivered his address to the World Congress in French, and he asked us to take note of the fact that he was not accustomed to speak in the French language. To-day I am in the same position as regards the English language, and I do not want to show less courage than did Lord Cadman. He is a professor, just as I am. I do not know whether professors always show courage, but I shall try to show it!

Only a few weeks have passed since the Paris Congress, and many of those present to-day have helped to increase the importance of the Second World Petroleum Congress, which was conducted by our friends and colleagues in such an excellent manner. We owe many thanks to the Institution of Petroleum Technologists for having put new life into the work of the Petroleum Congresses. We are all glad to see the new scientific bond uniting nations across continents and oceans. (Applause.) For that reason, I am especially charged to offer many thanks to the Institution in the name of the foreign guests.

I should now like to make a few scientific remarks, and, because my knowledge of the English language is insufficient for the purpose, I ask leave to speak in German.

*Speaking in German, Dr. Ubbelohde said :* At one time we were accustomed to measure the civilization and culture of nations by the average quantity of washing-soap consumed by each inhabitant. (Laughter.) Nowadays, we might equally well say that the civilization of a country is to be gauged by the amount of mineral oil products used, because the consumption of mineral oil is associated with many advances in civilization and culture. The position has always been a peculiar one, inasmuch, as while petroleum is obtained in a few countries only, it is used in all; thus it is not only the international commercial product *par excellence*, but has also caused a constant silent feud between producers and consumers in regard to quality and supply. One result of this, among others, is that not only the producing, but also the consuming countries have gone thoroughly, both scientifically and analytically, into the question of petroleum and its products; hence in all countries the science of petroleum has become a national, and consequently an international, science.

Recently, the basis of the mineral oil industry has begun to change, owing to the production of artificial mineral oils from coal, and consequently more countries than hitherto should gradually be in a position to produce mineral oils. My neighbour at this table, Mr. J. B. Kessler—who, as we all know, occupies an eminent position in the industry of petroleum obtained from natural sources—finds that artificial mineral oil is too dear, and he is right. It will be a long time before we spoil the prices of natural rock oil; but we want to co-operate with Mr. Delvin, the conjurer who, with his bird "Sally," has at this annual dinner conjured up many things out of nothing, and then you will see, Mr. Kessler! (Laughter.)

However, it is not only in countries which themselves have no natural resources of petroleum that the production of mineral oils from coal has been commenced; this is gradually becoming the case also in countries which possess oil-fields. The mineral oil industry is thus to a still greater degree than before becoming international, and consequently international scientific co-operation in our sphere is assuming still greater importance. It was really therefore an opportune measure to bring again into better co-operation and as closely as possible the scientific investigations made in the domain of mineral oils all over the world, as has been done by the Congresses held in London and in Paris, and that is why I again have to express thanks on behalf of all the foreign guests.

*Concluding in English, Dr. Ubbelohde said :* Not only our great interest in the international science of petroleum, but also the personal character of this annual dinner of the Institution of Petroleum Technologists, is bringing us together. We will try to keep these happy personal relationships and to hold to them. (Applause.) I beg to thank you, Professor Nash, for the kind way in which you have proposed this toast. (Applause.)

Ir. J. H. C. De Brey, who also responded, said: On behalf of my Dutch colleagues, and as representative of the Royal Institution of Engineers of the Netherlands, I avail myself with great pleasure of the opportunity afforded to me to give expression to our feelings of extreme gratitude for the brilliant reception which you have offered to us to-night.

We have already heard so many words of praise and appreciation to-night, that I really think I cannot do better than endorse everything which has been said in honour of our hosts, the Institution of Petroleum Technologists. I may add that we petroleum men from Holland have a special reason and an additional cause to be grateful to the Institution of Petroleum Technologists, because, as you will remember, in the spring of last year the Institution arranged a meeting in Holland, where they were the guests of our Royal Institution of Engineers. The meetings and discussions which took place are, I am sure, still fresh in the memory of those who took part in them, and I think that it must be a source of satisfaction to you who are members of the Institution of Petroleum Technologists to learn from me that the initiative which you took last year, when you crossed the Channel for the purpose of strengthening the bond between the petroleum technologists of both our countries, led to the birth of an idea which materialized a very short time afterwards for the founding in Holland, albeit on a small scale, of an organization which would be, so to speak, an equivalent of your so much admired Institution. In fact, the foundation of the Section for Petroleum Technology of the Royal Dutch Institution of Engineers can be considered as a direct result of your very welcome visit to Holland last year. (Applause.) We have to thank you for it, and I feel sure that in future both our organizations will work together and achieve results for the benefit of petroleum technology, whose humble servants we all are. (Applause.)

I notice that the *Petroleum Times* for 23rd May of last year gave an enthusiastic account of what happened during that meeting in Holland, but there is one point on which I would express my disagreement with the *Petroleum Times*. After many words of appreciation and praise of the Reception Committee in Holland, it stated : " It has to be confessed that the British character often causes us to overlook those little touches, so common on the Continent, which make such an impression and so much difference to the pleasure of foreign guests in our midst at conferences and such-like." I am glad that I can disagree with those words. This evening has proved once again that those little touches, which may be common on the Continent, are apparently a habit of all the members of this Institution of Petroleum Technologists. (Laughter and applause.)

The proceedings closed with the singing of the National Anthem.

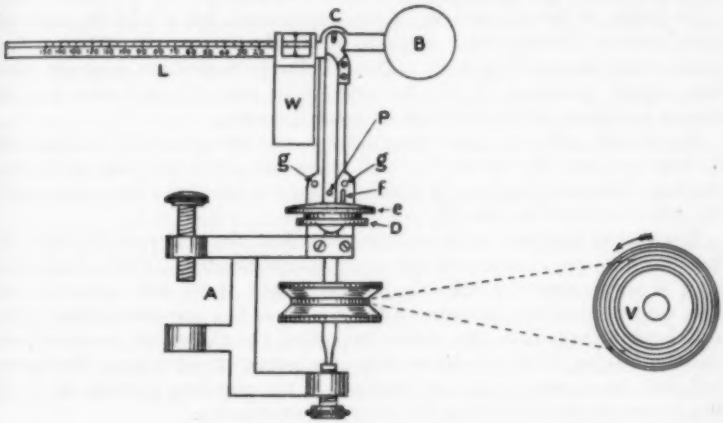
# McNAUGHT'S OIL TEST.*

*(Reprinted from "The Practical Mechanic and Engineers' Magazine," 1842.)*

THE Oil Test is an instrument for ascertaining the quality of oil, as applied to machinery or for burning. It shows exactly the different degrees of tenacity, and in what degree different oils lessen friction, or what the lubricating qualities of the oils submitted to trials are; and enables a person in a few minutes to ascertain with certainty the relative values of that he means to purchase, and to compare the stock with the sample he has made trial of.

## DESCRIPTION OF THE FIGURE.

A is a cramp with its screw for fixing the instrument; *P* is a pulley for driving the arbor; *D* is a piece of brass screwed on the top of the arbor,




McNAUGHT'S OIL TEST.

for holding the oil to be tried; the top of the arbor goes through the socket of the upper plate; these plates are turned perfectly true and flat, but do not touch each other. This is regulated by a small screw on the top of the socket of the upper plate, which can be screwed down, so as to prevent the plates touching each other, leaving only a thin film of oil between. As much oil must be put into the cup of the under plate as will just appear above the upper plate: the motion will cause the superfluous oil to fly off. *F* is a pin fastened to the top plate, which, when turned round against the sun, will come in contact with the pin *P*, and endeavour to carry it forward

* The apparatus described in the excerpt from *The Practical Mechanic and Engineers' Magazine* was presented to the Institution by Mr. J. Kewley. The Council loaned the apparatus to the Science Museum for the recent Exhibition on Lubrication, and it will remain as one of the permanent exhibits in the Museum.

towards the stop on the side next the cramp. The stops are to prevent its being carried too far out of the perpendicular. *W* is a sliding weight, being kept steady in any situation by a small spring. *C* is the centre upon which the lever runs, being supported in the upper part of the brass frame: the lever is divided into 150 equal parts. *B* is a counter-weight. When the mark upon the counter-weight corresponds with *o*, the graduated leg of the lever will be horizontal, and the leg *P* will be perpendicular, playing freely between the stops, without touching either of them, and is then in equilibrium. *V* is a pulley with six or eight grooves, varying about $\frac{1}{8}$ of an inch each; for the convenience of finding the desired speed and for immediate application, it is supposed to be fixed on the point of a turning lathe spindle; the cramp being fixed to the lathe rest, the rest will slide out or in, so as to answer the driving band, and the different sizes of the pulleys.

When the oil to be submitted to trial is put between the plates, and the apparatus set in motion, the sliding weight may be shifted above the graduated lever until it stands at some point; for instance, with good sperm oil, if it is brought to such a speed as to indicate 30 on the scale, then neat-foot, olive, and gallipolic oils will be about 60.

To judge of the correctness of the instrument, let a trial be made of equal parts of different oils. Suppose one of them to stand at 30, the other at 60; then the medium is 45. This will be the case if the mixtures have been equal; however, it will be sufficiently near to show that bad oil cannot be mixed with good without being detected.

As oils sold under the same name differ so much in quality, it is impossible to state precisely the speed that will make any given oil point to a given number; but as comparative trial is all that is wanted, every person will be able to do this for himself.

From what has been explained and described, the principle on which the instrument is constructed will be easily comprehended. Thus, if with one kind of oil the tenacity will only lift the weight at 20, and another at 40, it is evident that the tenacity of the former is but one-half of the latter, and lessens friction in the same proportion, as far as oil is concerned; thereby leaving it in the option of the proprietor of machinery whether he will save his money in oil, and waste it in the purchase of coals, or waste the power otherwise, besides the injury of machinery.

# CORRESPONDENCE.

*To the Editor.*

DEAR SIR,

When I concluded my paper in the *I.P.T. Journal*, 1937, **23**, 253, with the remark " . . . it is hoped that the publication of the results obtained will be of service to future investigators in this field," I certainly did not expect a response so soon.

I am, of course, aware that the above-mentioned paper by no means exhausted the possibilities of the subject, and I am pleased to see the interesting extension given by Messrs. Heinze and Marder in their paper "The Determination of the Ignitability of Diesel Oils on a Laboratory Scale."

Their exact application of my figures has impressed me very much, and has removed a slight misunderstanding which I had with regard to their ideas.

At the same time Messrs. Heinze and Marder's paper calls for some general comments, although I completely agree with its indication that more satisfactory results are obtained in our examples by applying the proposed correction for deviating " Kennziffer."

The discussion of Fig. 1 showed the need for making allowance for the molecular weight before drawing conclusions regarding the chemical composition of a hydrocarbon from a chemical constant, and the " Kennziffer " is introduced instead of the average molecular weight on the assumption that the latter is about proportional to it.

This is actually true only when moderate amounts of aromatic hydrocarbons are present, and is illustrated by Fig. A.

In this graph the " Kennziffer " is shown as a function of the mean molecular weight, and the highly aromatic oil, 1, shows a serious deviation from the line giving the general relation between " Kennziffer " and molecular weight. Since the correct engine cetene value of this oil can still be derived with considerable accuracy from the laboratory figures, it is clear that whatever may be the real significance of Heinze and Marder's correction, it is not merely a physical correction for deviating mean molecular weight.

Moreover, in my opinion, the calculation of the " Kennziffer " will only be completely reliable if the entire distillation curve can be obtained. When this is not possible, as, for example, in the case of the heavier fuels, we can only calculate the " Kennziffer " from the experimental portion of the distillation curve if this curve is symmetrical about the 50 per cent. boiling point. We have then to deal with single fractions as we had with the oils I investigated and referred to as nos. 3, 11 and 8. In these we calculated the " Kennziffer " to be 294·8, 313·1 and 296·6° C.

It is important to remember, however, that most of the heavier diesel oils cannot be treated in this way, on account of the probability that they are mixtures of gas oil and residue, and are therefore likely to have non-symmetrical distillation curves. Further, I consider that a mixture of hydrocarbons such as constitutes an oil is only poorly defined by one or two constants. The fact that one or two constants often fairly well define an oil shows that there is probably no important variation between the com-

positions of most oils, but, at the same time, it seems unsatisfactory to generalize in the manner proposed by Heinze and Marder.

Thus, although there is doubtless a tendency to improve results by applying a " Kennziffer " correction, it should not be forgotten that, in practice, it is not the average deviation which is of most importance, but the maximum deviation. The maximum deviation determined from Heinze and Marder's

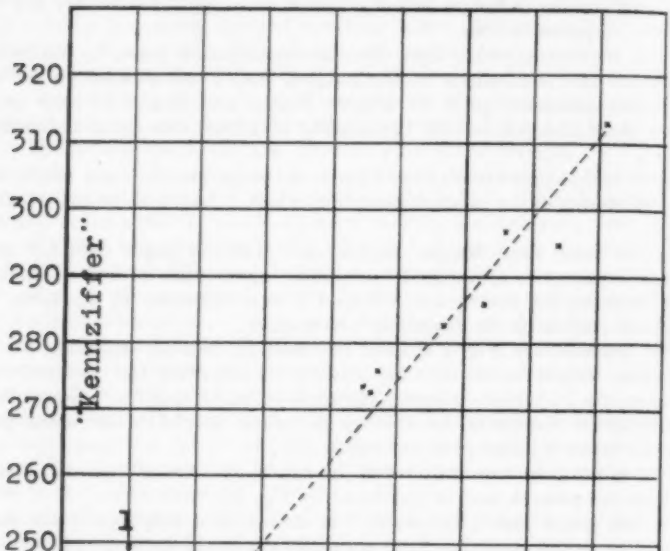



FIG. A.

graph, Fig. 3, both from the specific parachor and the diesel index, is 6½ cetene numbers—a value only slightly different from the 7 cetene numbers mentioned for the uncorrected diesel-index method.

Summarizing, although the application of a " Kennziffer " correction is of some practical interest, and while I shall myself probably apply such a correction in future to improve results slightly, I cannot agree with the general tendency of Messrs. Heinze and Marder's work in this direction, since I consider it to be wrong to attempt to specify such a complicated material as a fuel oil by so few constants as are used by Heinze and Marder.

I am, Yours faithfully,

D. J. W. KREULEN.

*Laboratorium Glückauf,*
*3e Katendrechtsche Hoofd*, 7
*Rotterdam* (*z*).

*October*, 1937.

# OBITUARY.

## PAUL DE CHAMBRIER.

PAUL DE CHAMBRIER was born in Bevaix, Switzerland, in 1866. On leaving the Ecole Polytechnique in Zurich he joined the Pechelbronn Mines as a Chemist on 15th October, 1892, where he had a rapid and spectacular career. In 1894 he was appointed Technical Director, and in 1906, when the Pechelbronn Mines were transferred to German administration, he accepted the post of Director General of the new company, "Vereinigte Pechelbronner Oelbergwerke," which later became an associated Company of the Deutsche Erdoel A.G. He held this post until 1918.

With the inauguration of the new French Company, "Pechelbronn S.A.E.M.," Paul de Chambrier was offered the post of Consulting Engineer, a post which he maintained until 1925, when he left Alsace altogether and retired to Switzerland.

During his connection with the Pechelbronn Mines, Paul de Chambrier developed and perfected a number of technical improvements, the most remarkable of which was the method of winning petroleum by means of shafts and galleries. This method, which rendered possible the recovery of oil remaining in the bed after exhaustion by boring, was successfully applied to the petroleum deposits in Alsace. It was a paper on this subject read to the Institution on 15th February, 1921, which won him the Redwood Medal in 1925.

In the same year the French Government awarded him the title of Knight of the Legion of Honour, and he was also elected an Honorary Doctor of the University of Neuchâtel.

Paul de Chambrier is the author of many books on Pechelbronn, of which the most important is "The History of Pechelbronn from 1498 to 1918."

With his death on 15th September, 1937, at the age of 70, the Institution has lost one of its most illustrious members.

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# THE PRINCIPLES OF SOLVENT DEWAXING. PART II: EQUILIBRIA AND COMPUTATIONS FOR DOUBLE SOLVENT SYSTEMS.*

By M. Ba Thi, B.Sc., A.I.C. (Student Member), T. G. Hunter, Ph.D., A.R.T.C., A.I.C. (Member), and A. W. Nash, M.Sc., M.I.Chem.E., M.I.Mech.E. (Member).

In a previous paper [1] it was shown how phase-rule graphical methods could be applied to equilibria representation and to computations for dewaxing processes employing a single solvent completely miscible with the oil at the operating temperature. A recent development in dewaxing processes is the employment of solvents consisting of mixtures of two or more components, as for example the benzol–acetone dewaxing process. This paper is an attempt to represent equilibria and devise computations for solvent systems employing a double solvent completely miscible with the oil at the operating temperature.

The equilibria involved in such processes are those between a solid phase or phases (paraffin wax), a complex liquid hydrocarbon mixture (oil), and two solvent liquids. Before considering such a system, standard methods of representing equilibrium in the simpler quaternary system of one pure solid component and three pure liquid components will be described.

## Equilibrium in a Four Component Solid–Liquid System.

Increasing the number of components in a system increases the difficulty of graphically representing equilibrium relationships. The relationships in a system of three independently variable components may be conveniently represented in two dimensions by plotting on an equilateral triangular diagram. A system of four independently variable components can only be represented in a three-dimensional figure. A four-component system is usually represented by a space model of a tetrahedron or an equilateral triangular prism.

A system consisting of four components *A*, *B*, *C*, and *D* may be regarded as a combination of the four ternary systems, *A–B–C*, *A–B–D*, *A–C–D*, and *B–C–D*, or as a combination of the six binary systems *A–B*, *A–C*, *A–D*, *B–C*, *B–D*, and *C–D*. In view of the usefulness of the equilateral triangle in representing the ternary system it is obvious that four such triangles, arranged to form a regular tetrahedron, will be suitable for representing a system of four components.

Fig. 1 shows a tetrahedron in perspective, the angles *A*, *B*, *C*, and *D* of which represent the respective pure components. The six possible binary systems will be given by the lines joining the angular points, and

* Paper presented for Discussion at the One Hundred and Seventy-seventh General Meeting of the Institution of Petroleum Technologists, November 9th, 1937.

the four possible ternary systems will be given by the four bounding triangular surfaces, while all possible quaternary mixtures of the components may be represented by points inside the space enclosed by the triangular boundary surfaces.

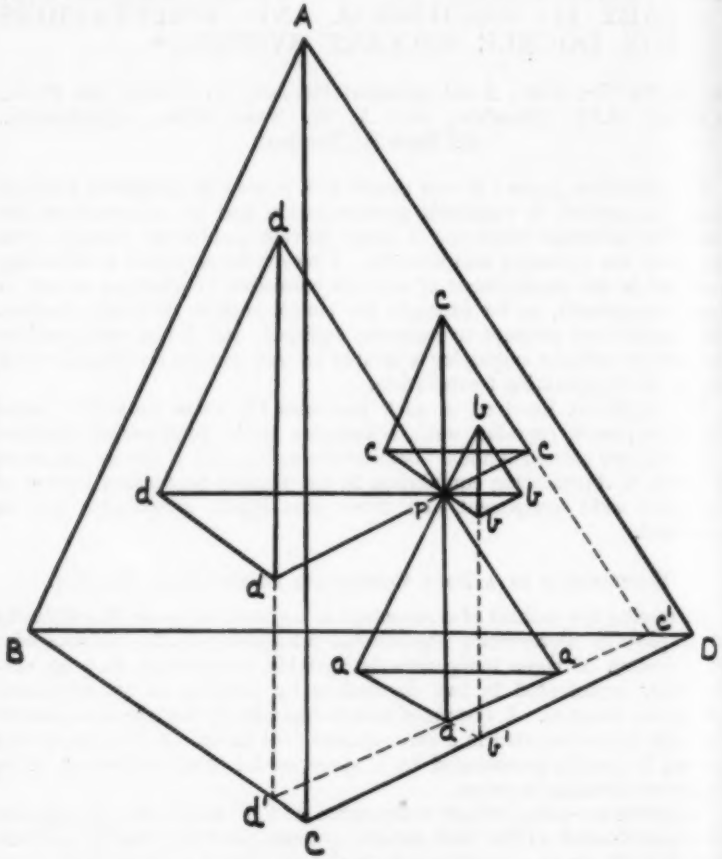


FIG. 1.

As in the case for the ternary system, each side of a triangle may be taken to represent 100 units of weight composition. If, through any point $P$, within the tetrahedron, parallels to the respective edges are drawn to meet the bounding surfaces, four regular tetrahedra will result as shown in Fig. 1. These four tetrahedra have a common apex $P$, and lengths of edge, $Pa$, $Pb$, $Pc$, and $Pd$. From the construction of the dotted lines in Fig. 1 it is obvious that

$$Pa + Pb + Pc + Pd = aa + ab' + ac' + ad' = c'd' + ab'.$$

It can be easily proved geometrically that

$$c'd' + ab' = CD = 100 \text{ units.}$$

If the weight percentage of components $A$, $B$, $C$, and $D$ are proportional to the lengths $Pa$, $Pb$, $Pc$, and $Pd$ respectively, then the composition of this quaternary mixture is represented by point $P$. Therefore, according to the position of such a point inside the tetrahedron, every possible mixture of the components may be similarly represented.

A model of equilibrium relationship for the special case of one solid and three liquid components forming a two-phase system at some temperature below the melting point of solid $A$ and above the freezing points of liquids $B$, $C$, and $D$ will take the form of Fig. 2.

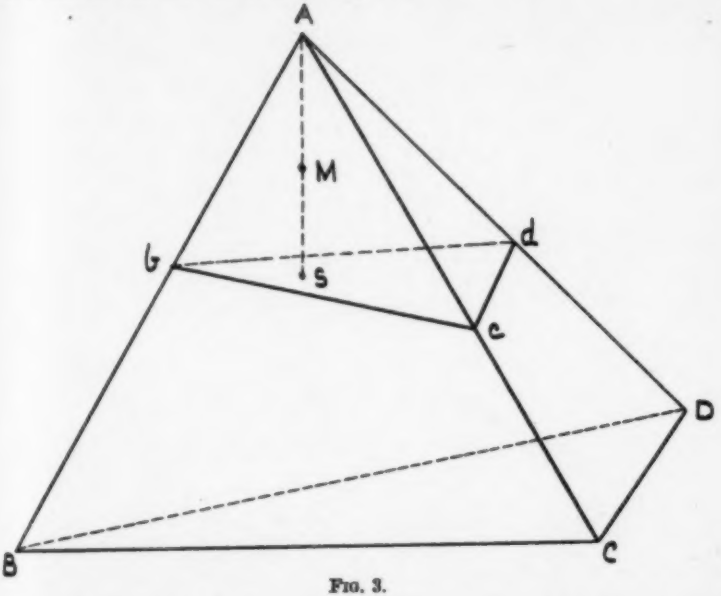


FIG. 3.

In this figure the points $b$, $c$, and $d$ on the edges $AB$, $AC$, and $AD$ represent, respectively, the solubilities or saturated solutions of solid $A$ in pure liquid $B$, pure liquid $C$ and pure liquid $D$. The curves $bc$, $cd$, and $db$ represent, respectively, the solubilities or saturated solutions of solid $A$ in the liquid mixtures $B$–$C$, $C$–$D$, and $D$–$B$. These curves are ternary saturation curves. The quaternary equilibrium is represented by the surface $bcd$. Each point on $bcd$ represents a saturated solution of solid $A$ in the liquid mixture $B$–$C$–$D$. All mixtures the composition of which may be represented by points within the space $BCDbcd$ are unsaturated liquids, and exist as single homogeneous liquid phases. All mixtures the composition of which may be represented by points within the space $Abcd$ are supersaturated and must separate into two phases, solid phases consisting of pure $A$, and saturated liquid phases with compositions

represented by points on the saturation surface *bcd*. The mixture represented by point *M* in Fig. 3 would separate into solid *A* and a saturated liquid of composition represented by point *S*. The ratio of solid *A* to liquid *S* would be given by the ratio *SM*/*MA*. The line *AMS* is a tie-line joining the two phases, solid *A* and liquid *S*, which are in equilibrium. Since all tie-lines pass through a common point, apex *A*, they are usually omitted in the space model.

In simple cases a perspective drawing of a tetrahedron is easily made, but affords only a qualitative description of equilibria. In practice it is therefore usual to work with projections of the tetrahedron on a plane in which plotting may be carried out quantitatively. From projections in two different directions the space model may be reconstructed if desired.

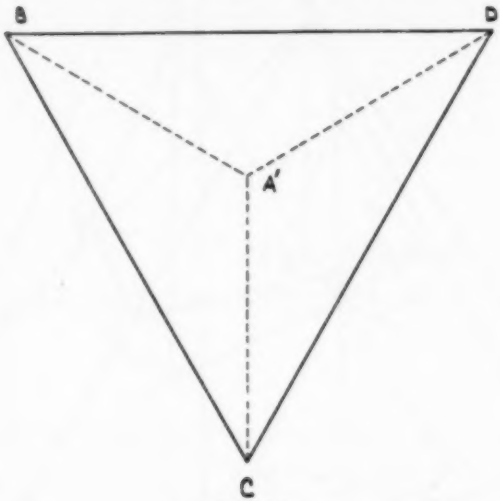


FIG. 4 (*a*).

Projections made orthogonally, *i.e.* at right angles, to selected planes are most useful. Two orthogonal projections are commonly employed.

In the first, the tetrahedron and space figure within it are projected upon the base plane by means of parallel lines perpendicular to the base. In Fig. 4 (*a*) the vertex *A* of the tetrahedron has been projected to give a point *A'* upon the base plane *BCD* perpendicularly below it. The three lateral edges have been projected to give the three lines *A'B*, *A'C*, and *A'D*.

In Fig. 4 (*b*) the projection of the quaternary saturation surface of Fig. 2 is illustrated. Points *b'*, *c'*, and *d'* are projections of the points *b*, *c*, and *d* which give the compositions of the saturated binary solutions. Lines *b'c'*, *c'd'*, and *d'b'* are projections of the ternary saturation curves *bc*, *cd*, and *db*. In order to construct this projection it is necessary to know the relation between the position of a point in the tetrahedron and the position of its projection on the triangular base plane. The position of any point *P* within the tetrahedron may be defined by the weight percentages, *w*,

$x$, $y$, and $z$ of the four components $A$, $B$, $C$, and $D$. The position of its projection $p$ can be defined by the distances of $p$ from the three sides of the base triangle, say $x'$, $y'$, and $z'$. From its position in the triangle $BCD$ it can be considered to represent a ternary mixture of $x'$, $y'$ and $z'$ weight percentages of $B$, $C$, and $D$. The relations between $w$, $x$, $y$, $z$ and $x'$, $y'$, $z'$ can from geometrical considerations be shown to be $x' = x + w/3$, $y' = y + w/3$, and $z' = z + w/3$. The position of the projection is therefore located by the following rule. The actual percentage, $x$, of $B$ in the quaternary mixture is increased by one-third the percentage of $A$, *i.e.* by $w/3$, and similarly for $y$, and $z$ the percentages of $C$ and $D$. The position of the projection on the base plane is then $(x + w/3)$ per cent of $B$, $(y + w/3)$ per cent. of $C$ and $(z + w/3)$ per cent. of $D$.

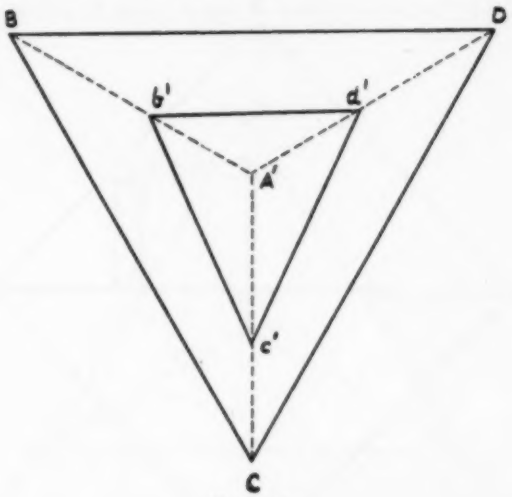


FIG. 4 (*b*).

The second projection is obtained in the following way. When the base $BCD$ of the tetrahedron in Fig. 5 rests upon the ground plane, the vertex $A$ is perpendicularly above the centroid of the base triangle. If the tetrahedron is rotated about its edge $CD$, which remains on the ground plane, until the two vertices $B$ and $A$ are equidistant above the ground plane, then the edge $BA$ is parallel to the ground plane. The tetrahedron in this position is now projected perpendicularly upon the ground plane, as shown in Fig. 6. The line $B'A'$ is the projection of the edge $BA$ and is equal in length to the edge $BA$, since this edge is parallel to the ground plane. The line $C'D'$ is the projection of the edge $CD$ and is equal to it in length, since this edge $CD$ is also parallel to the ground plane. The two lines $B'A'$ and $C'D'$ bisect each other at right angles and form the diagonals of a square $B'D'A'C'$, the four sides of which are the projections of the remaining four edges of the tetrahedron. The position of any point $P$ within the tetrahedron can be defined as before by the weight percentages

$w$, $x$, $y$, and $z$ of the four components $A$, $B$, $C$, and $D$. The position of its projection $p$, can be defined by the distances of $p$ from the two diagonals $B'A'$ and $C'D'$, which may be regarded as axes of rectangular co-ordinates. If the distance $pb$ of the point $p$ from the axis $C'D'$ in Fig. 7 is called $a$, and the distance $pd$ from the axis $B'A'$ is called $e$, then the relationships between $a$, $e$ and $w$, $x$, $y$, $z$ are

$$a = \frac{w - x}{2} \text{ and } e = \frac{z - y}{2}$$

In plotting these points the co-ordinate $a$ is measured parallel to the axis $OA'$ and the co-ordinate $e$ is measured parallel to the axis $OD'$. Regard

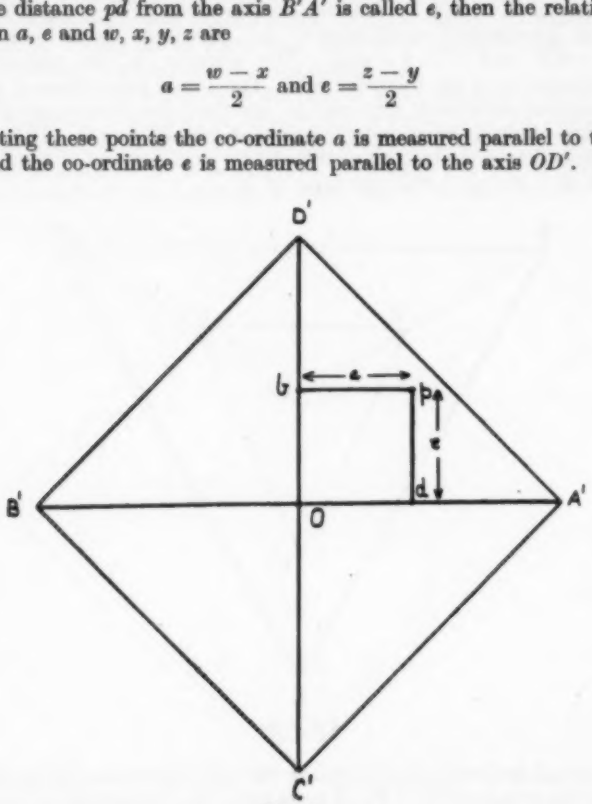


Fig. 7.

must be given to the algebraic sign of these co-ordinates. If $w - x$ is negative, then the distance $\frac{w - x}{2}$ is negative and must be measured parallel to $OA'$ in the negative direction $O$ to $B'$. Similarly if $\frac{z - y}{2}$ is negative, it must be measured in the direction $O$ to $C'$.

In Fig. 8 the second method of projection is illustrated by the projection of the quaternary saturation surface of Fig. 2. Points $b'$, $c'$, and $d'$ are projections of the points $b$, $c$, and $d$ which give the compositions of the saturated binary solutions. Lines $b'c'$, $c'd'$, and $d'b'$ are projections of the ternary saturation curves $bc$, $cd$, and $db$.

### Oil–Wax–Solvent/Solvent Equilibria.

Approximate representation of equilibrium in an oil–wax–solvent/solvent system may be obtained by assuming the oil and wax each to behave as single pure components. Normal operating conditions for dewaxing processes are such that the solvent and oil are completely miscible and liquid. The lowest temperature to be considered, therefore, must normally be higher than the freezing point of the wax-free oil, and also higher than the freezing point of both solvents. Both the solvents and the oil used are assumed to form a single homogeneous liquid phase over the whole temperature range considered. Under the conditions to be employed only two phases, liquid and solid, exist. Since the total oil present in the system will, under the restricted range of conditions to be employed, always be in the liquid phase, it may be safely treated as if it were a single

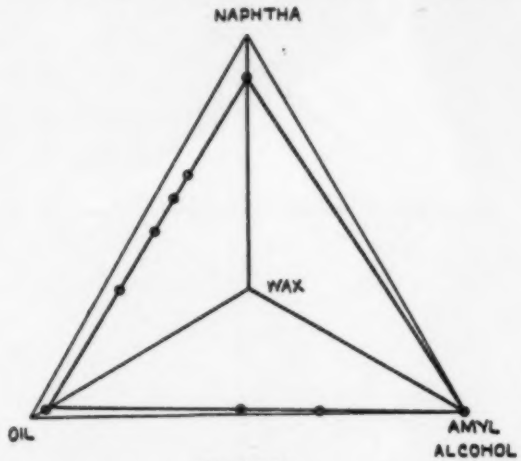


Fig. 10 (*a*).

pure component. This assumes, of course, that no solid solutions of oil or oil and solvents in wax exist under the given conditions. The wax, however, is usually distributed between two phases, solid phase and liquid phase. Since wax is a complex material, the composition of the wax in both phases must vary, and the fact that wax is regarded throughout as if it were a single pure component introduces an error. So far this quantitative error involved has been found to be small and of little importance in technical calculations and computations.

The operating conditions normally prevailing in dewaxing processes restrict the equilibrium in the majority of instances to the special case of one solid, three liquid components giving rise to two phases, one solid phase and one liquid phase. The equilibrium representation of this system will be of the type already discussed and illustrated in Fig. 2, 4 (*b*), and 8, the four components *A*, *B*, *C*, and *D* of these figures being replaced by wax, oil and the two solvents. The space model representing the

equilibrium at 50° F. for the system wax, melting point 108° F., Anglo-Iranian second cooled blue oil, amyl alcohol and naphtha, is shown in Fig. 9. The two projections of this model are given in Fig. 10 (*a*) and (*b*).

In Fig. 9 the ternary saturation curves *bc* for wax-oil-amyl alcohol, *cd* for wax-amyl-alcohol-naphtha, and *db* for wax-naphtha-oil are straight lines, and the quaternary saturation surface *bcd* is a smooth inclined plane. This plane is inclined from *bd* down towards *c*, which is almost coincident with the amyl alcohol apex of the tetrahedron.

In a double solvent dewaxing process a known oil–wax mixture is treated with a solvent consisting of a known mixture of two solvents $S_1$ and $S_2$ in the ratio $S_1/S_2 = R$. As previously explained, under the operating conditions employed, the solvent, a mixture of $S_1$ and $S_2$, always

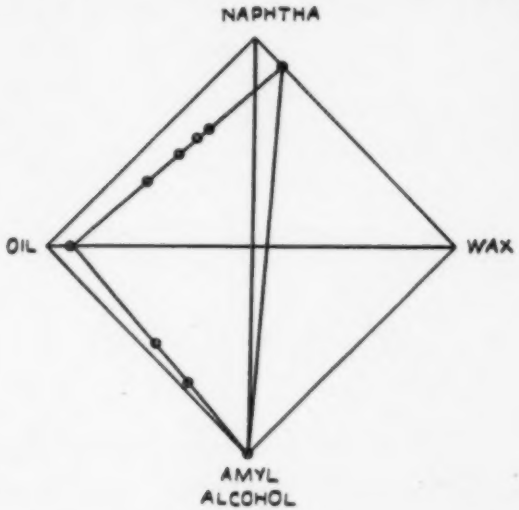


FIG. 10 (*b*).

remains in the liquid phase. Any liquid phase formed in the process therefore always contains $S_1$ and $S_2$ in their original ratio $S_1/S_2 = R$.

In order to carry out dewaxing computations using either of the two projection diagrams, it is first necessary to locate a curve or line representing a saturated solution on the quaternary saturation surface where every point on this curve indicates a $S_1/S_2$ ratio equal to $R$—that is, a constant solvent/solvent ratio saturated solution curve. In Fig. 11 the point $M$ represents a solvent mixture of $S_1$ and $S_2$ in the ratio $S_1/S_2 = R$. The plane $WOM$ is a triangular shaped plane inclined at an angle to the base of the tetrahedron. This plane $WOM$ intersects the quaternary saturation surface. The intersection between the triangular plane $WOM$ and the inclined plane which is the quaternary saturation surface is the straight line $PQ$. For all points lying in the triangular plane $WOM$ which represent mixtures containing two solvents, the two solvents,

FIG. 6.




FIG. 5.




FIG. 2.

[To face p. 714.

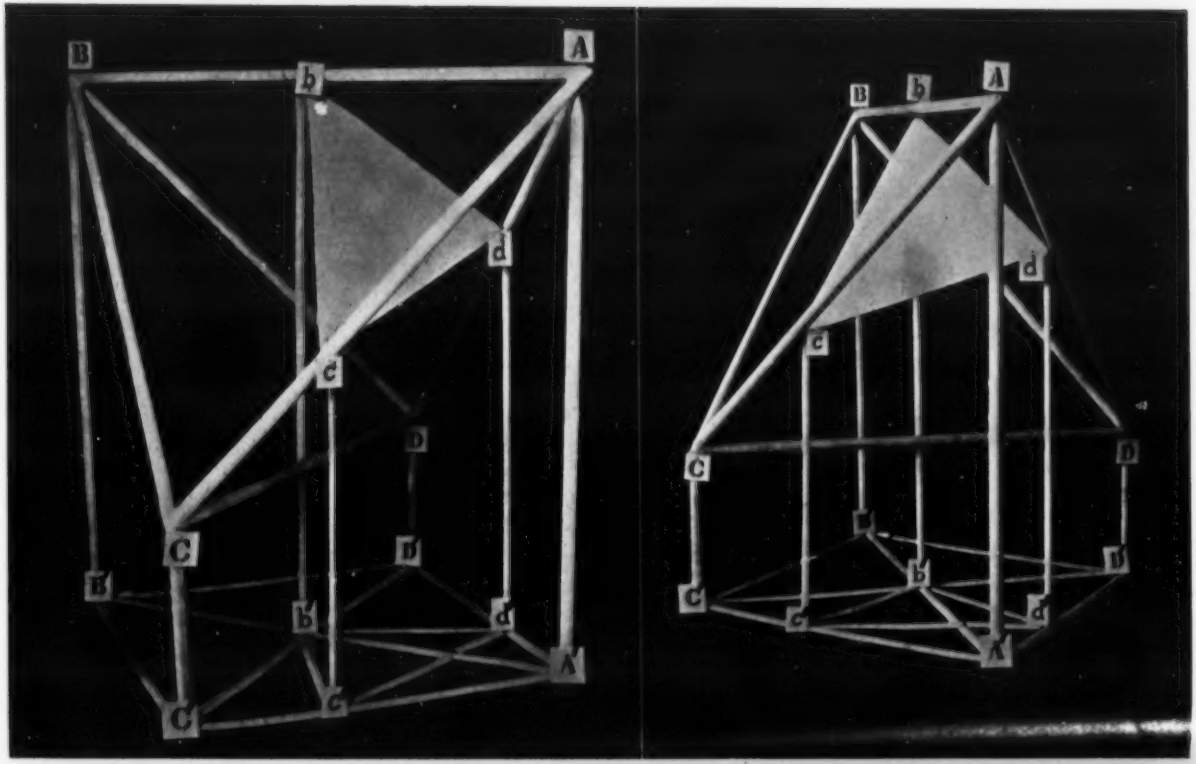


Fig. 8.

Fig. 8.

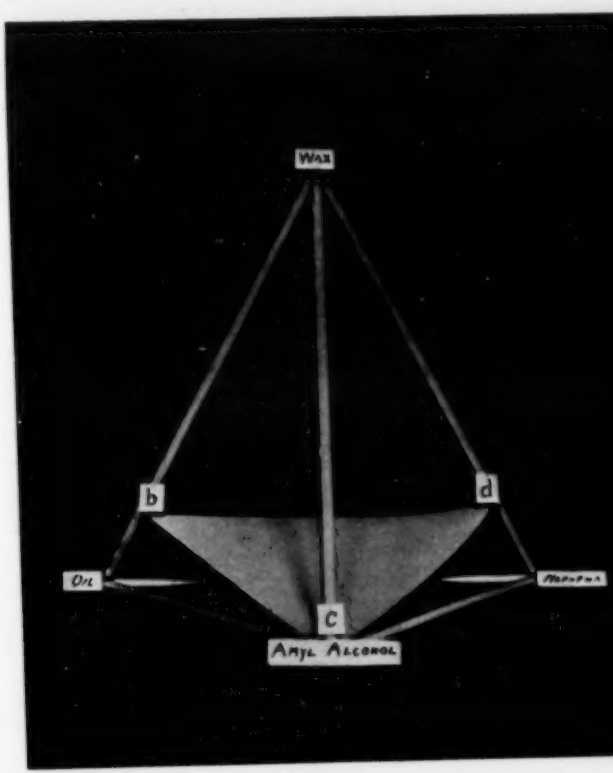


Fig. 9.

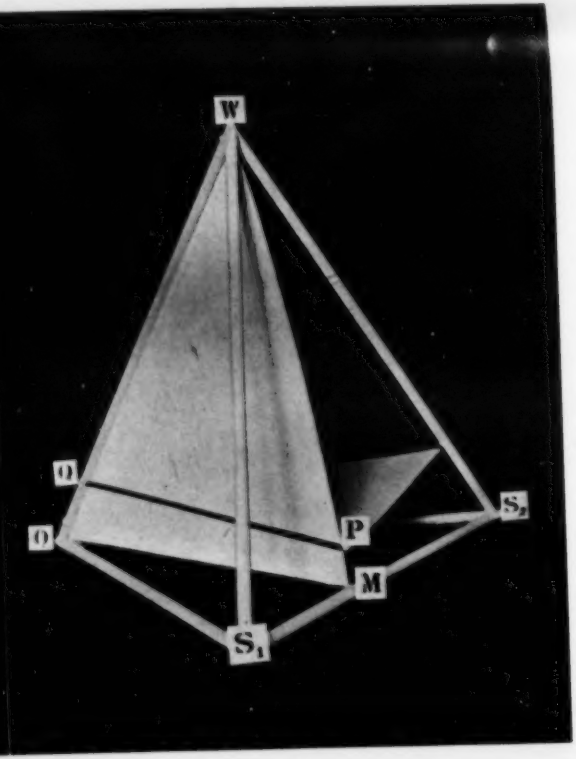


Fig. 11.

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$S_1$ and $S_2$, are always present in the proportion $S_1/S_2 = R$. $PQ$ is therefore a curve or line giving the composition of saturated solutions of constant

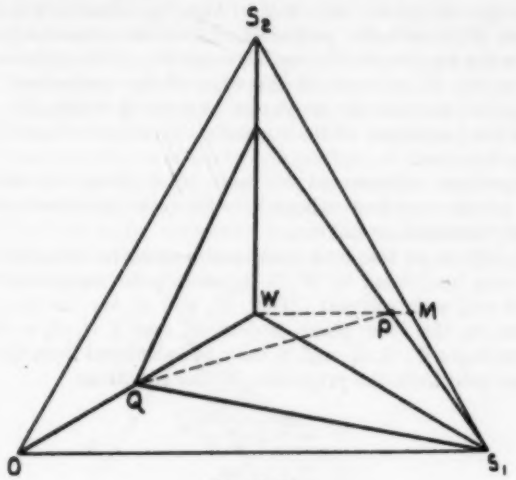


FIG. 12 (a).

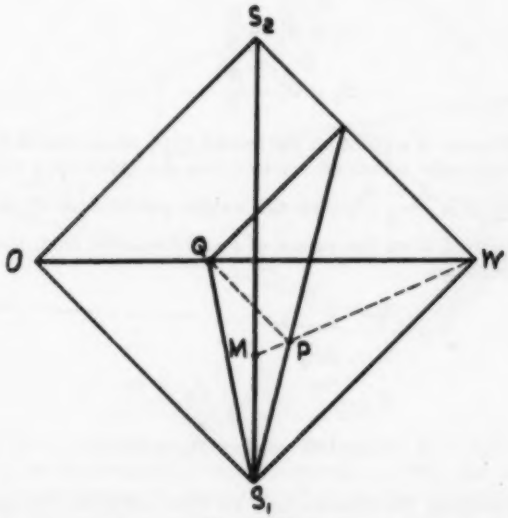


FIG. 12 (b).

solvent/solvent ratio. When the quaternary saturation surface is an inclined plane, the curve of intersection is a straight line. This is the case in the example illustrated in Fig. 11, and here $PQ$ is readily obtained from

the intersections $P$ and $Q$ of the lines $WM$ and $WO$ with the edges of the quaternary saturation surface. On the two projections in Fig. 12 ($a$) and ($b$) the point $P$ is obtained by locating $M$ on the line $S_1S_2$; joining $WM$ gives the projection of the line $WM$ of Fig. 11. The intersection of the projected line $WM$ with the projected edge of the quaternary saturation surface gives the projection of point $P$, as shown. The projected line $WO$ intersects on Fig. 12 ($a$) and ($b$) the edge of the quaternary saturation surface at $Q$, this point is the projection of point $Q$ of Fig. 11. Joining $P$ and $Q$ gives the projection of the constant solvent/solvent ratio saturated solution line required.

The composition represented by any point lying on either of the projections of the constant solvent/solvent ratio saturated solution line may be easily obtained as follows.

The composition of the four component mixture represented by any such point may be defined by $W$, $O$, $S_1$, and $S_2$ the weight percentages of the wax, oil and each solvent. If $O'$, $S_1'$, and $S_2'$ are the co-ordinates of such a point on the base plane projection, and if $S_1/S_2 = R$, then the weight percentages $W$, $O$, $S_1$, and $S_2$ may be calculated from the values $O'$, $S_1'$, and $S_2'$ as read from the projection by the equations

$$W = \frac{3(S_1' - RS_2')}{1 - R}$$

$$O = O' - \frac{W}{3}$$

$$S_1 = S_1' - \frac{W}{3}$$

$$S_2 = S_2' - \frac{W}{3}$$

If the co-ordinates of a point on the second type projection of the constant solvent/solvent ratio saturated solution line are given by $e$ and $f$ where $e$ is $\frac{W - O}{2}$ and $f$ is $\frac{S_1 - S_2}{2}$, then the weight percentages $W$, $O$, $S_1$, and $S_2$ may be calculated from the values of $e$ and $f$ as read from the projection by the relationships

$$S_2 = \frac{2f}{R - 1}$$

$$S_1 = RS_2$$

$$W = \frac{100 - (S_1 + S_2) + 2e}{2}$$

$$O = 100 - (S_1 + S_2 + W)$$

## Experimental Determination of the Equilibrium Diagram.

Convenient methods of obtaining the equilibrium diagrams, namely, isothermal filtration, cloud-point measurements, and average wax solubility measurements, have been discussed in detail in a previous paper.[1] The data for constructing the ternary saturation curve for the wax-oil-

naphtha system of Figs. 9 and 10 were obtained by the cloud-point method. All other data were obtained by the isothermal filtration method.

If the surface giving the composition of quaternary saturated solutions is a plane and the bounding edges of this plane giving the composition of ternary saturated solutions are straight lines, then only the three points giving the composition of the binary saturated solutions need be determined. The three points so obtained may then be plotted on either of the two projections and joined by straight lines to give the complete projection of the saturation surface. In the majority of cases so far examined it has been found that the composition of the ternary saturated solutions can be represented by a straight line and the composition of the quaternary saturated solutions can be represented by a plane. It would appear from the data so far available that at low equilibrium temperatures all ternary saturation curves are straight lines and all quaternary saturation surfaces are plane surfaces.

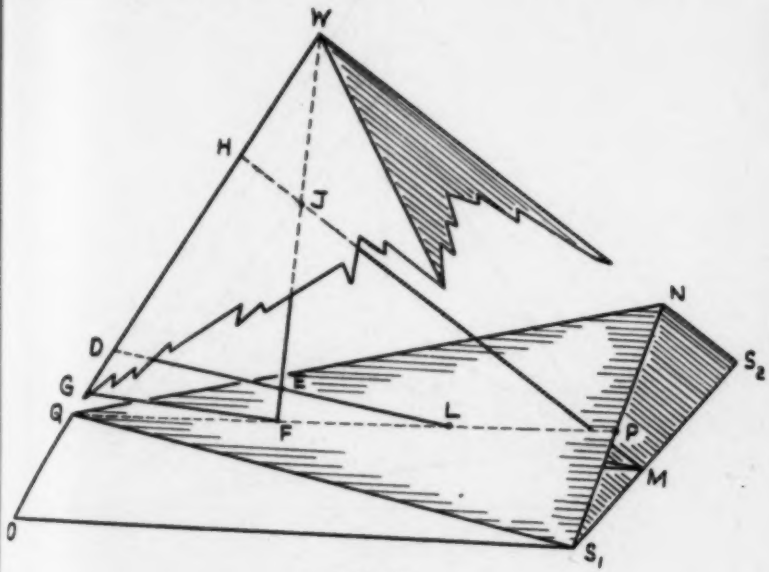


FIG. 13.

## DEWAXING COMPUTATIONS.

In Fig. 13 the equilibrium isotherm in the system wax, oil, solvent $S_1$ and solvent $S_2$ is represented by the plane surface $QNS_1$, the tetrahedron being cut away to expose to view the whole of this saturation surface. The point $M$ represents a solvent mixture of $S_1$ and $S_2$ in the ratio $S_1/S_2 = R$, and the broken line $PQ$ is the constant solvent/solvent ratio saturated solution line. If at the equilibrium temperature a solvent mixture of composition $M$ is added to any given wax-oil mixture, say of composition represented by point $D$, then the composition of all possible

mixtures of $D$ and $M$ must lie along the line $DM$. This line $DM$ intersects the saturation surface $QNS_1$ in the point $L$ which lies on the constant solvent/solvent ratio saturated solution line $PQ$. The section $DL$ of the line $DLM$ lies above the surface $QNS_1$, and the section $LM$ of the line $DLM$ lies below it. All mixtures of $M$ and $D$ which can be represented by a point on the line $DL$ fall within the two-phase (a co-existing solid and liquid phase) space $WQS_1N$ and all mixtures which can be represented by a point on the line $LM$ fall within the one-phase, liquid phase, space $QNS_2S_1O$. If to the mixture $D$ is added mixture $M$ in amount such that the ratio of mixture $M$ to mixture $D$ is $R_1$, then the composition of the

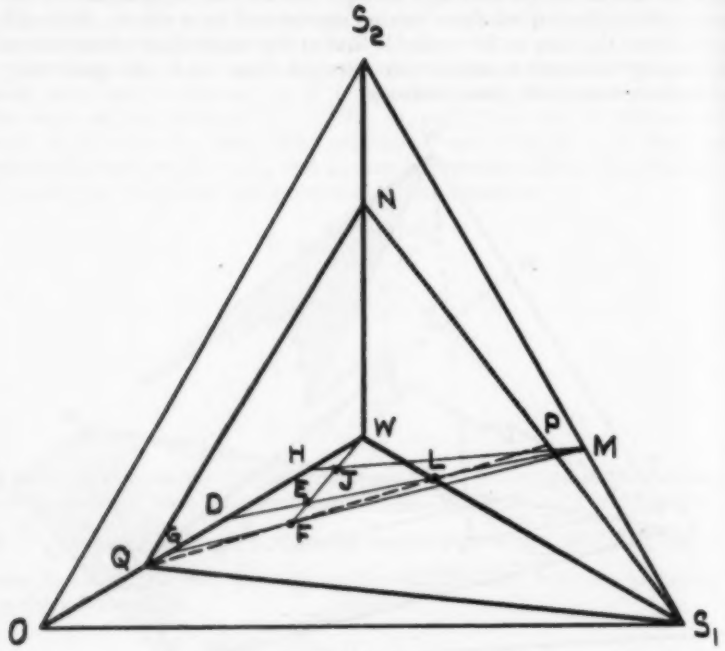


FIG. 14 (a).

resultant mixture is given by point $E$, where $DE/EM = R_1$. Since the point $E$ falls within the two-phase space $WQS_1N$, then the mixture represented by this point must exist as two phases, a solid phase $W$ and a liquid phase of composition $F$, the point $F$ being located by the intersection of the line $WE$ with the saturation surface $QNS_1$. Further, the point $F$ must be on the constant solvent/solvent ratio saturated solution line $PQ$. The ratio of solid phase $W$ to saturated liquid phase of composition $F$ in the resultant mixture must be $FE/EW$. If the mixture of solid phase $W$ and liquid phase $F$ are separated by filtration, the cake obtained will probably consist of the solid phase $W$, together with a small quantity of mechanically held liquid phase of composition $F$. The composition of this cake (a

mixture of solid phase and mechanically held liquid phase) must be represented by a point somewhere on the line *WEF*. Suppose the composition of the cake is known and is given by point *J*, then the yields of actual cake and filtrate can be obtained from the ratio *FE*/*EJ*, which is the ratio of cake to filtrate. The composition of the cake after removing all solvent $S_1$ and $S_2$ must be given by the intersection of the line passing through *M* and *J* with the side *WO* of the tetrahedron and will be given

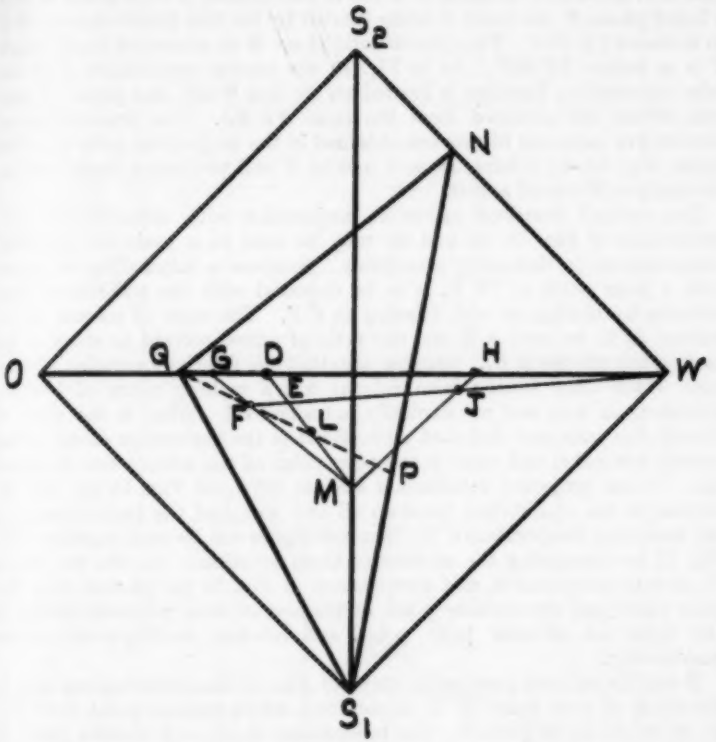


FIG. 14 (*b*).

by point *H*. Similarly the composition of the filtrate after removal of all solvents $S_1$ and $S_2$ must be given by the intersection of the line passing through *M* and *F* with the tetrahedron edge *WO* and will be point *G* in Fig. 13.

The two projections of the equilibrium surface of Fig. 13 are illustrated in Fig. 14. $QNS_1$ is the projection of the saturation surface and the line *PQ* is the projection of the constant solvent/solvent ratio saturated solution line where, as at point *M*, $S_1/S_2 = R$. The line *DM*, giving the composition of all possible mixtures of wax-oil mixture *D* and solvent mixture *M*, is located and obtained on the projections by joining *D* and

*M*. The intersection on the projections of *DM* and *PQ* gives the point *L* which is the intersection of *DM* with the saturation surface $QNS_1$. All mixtures of *D* and *M* which can be represented by points on *DL* in Fig. 14 (*a*) and (*b*) consist of two co-existing phases, solid phase *W* and a liquid phase, all mixtures represented by points on *LM* consist of one liquid phase only. A mixture of *M* and *D* in the ratio $M/D = R_1$ is represented in the projections by point *E* on the line *MD*, where $DE/EM = R_1$. The mixture represented by point *E* exists as two phases, a solid phase *W* and a liquid phase *F*, the point *F* being located by the line drawn through *WE* to intersect *PQ* at *F*. The ratio of solid phase *W* to saturated liquid phase *F* is as before *FE/EW*. As in Fig. 13 the known composition *J* of the cake obtained on filtration is located on the line *WEF*, and yields of cake and filtrate are obtained from the ratio *FE/EJ*. The composition of solvent-free cake and filtrate are obtained in the projections as in the solid figure, Fig. 13, by joining *M* to *J* and to *F* and producing these lines to cut the line *WO* in *H* and *G*.

The method described above in conjunction with either of the two projections of Fig. 14 (*a*) and (*b*) may be used as a basis for graphical computations in dewaxing operations. Suppose a lubricating oil stock with a pour point of 73° F. is to be dewaxed with the addition of two solvents by chilling to and filtering at *t*° F. The ratio of solvent $S_1$ to solvent $S_2$ to be used is *R* and the ratio of mixed solvent to stock to be used in the process is $R_1$. Suppose also that the filtering operation gives a cake which after freeing from solvent has a melting point of 104° F., consisting of wax and mechanically entrained oil. What is the yield of solvent-free cake and dewaxed oil? What is the percentage of oil in the solvent-free cake, and what is the pour point of the solvent-free dewaxed oil? If the projected equilibrium surface $QNS_1$ of Fig. 14 (*a*) and (*b*) represents the equilibrium between oil and wax and the two solvents at the dewaxing temperature *t*° F., then this figure can be used together with Fig. 15 for computing the answers to these questions. On the two scales of oil–wax composition, and temperature of Fig. 15 are plotted both the pour point and the melting point of varying oil–wax mixtures shown in the figure as oil–wax pour point, and oil–wax melting-point curves respectively.

From the oil–wax pour-point curve of Fig. 15 the percentage of wax in the stock of pour point 73° F. is obtained, which enables point *D* of Fig. 14 (*a*) or (*b*) to be located. The relationship $S_1/S_2 = R$ enables point *M* to be located, and hence the constant solvent/solvent ratio saturated solution line *PQ* to be determined as described previously. The ratio mixed solvent to stock equal to $R_1$ enables point *E* to be fixed, and the tie line *WEF* may then be drawn. The composition of the solvent-free cake may be taken as the composition of the oil–wax mixture having the same melting point, and from the oil–wax melting point curve of Fig. 15 the composition of the oil–wax mixture having a melting point of 104° F. is obtained, which enables point *H* in Fig. 14 (*a*) and (*b*) to be located. Point *J* is then obtained as the intersection of lines *HM* and *WEF*. The ratio of actual cake to actual filtrate obtained from the filtering operation is then given by the ratio *FE/EJ*. The composition of the solvent-free filtrate is given by point *G* obtained by the construction already described. The

ratio solvent-free cake to solvent-free filtrate is then given by $GD/DH$ and the pour point of the dewaxed oil—that is, solvent-free filtrate—is the pour point of the oil–wax mixture of composition $G$ as given by Fig. 15.

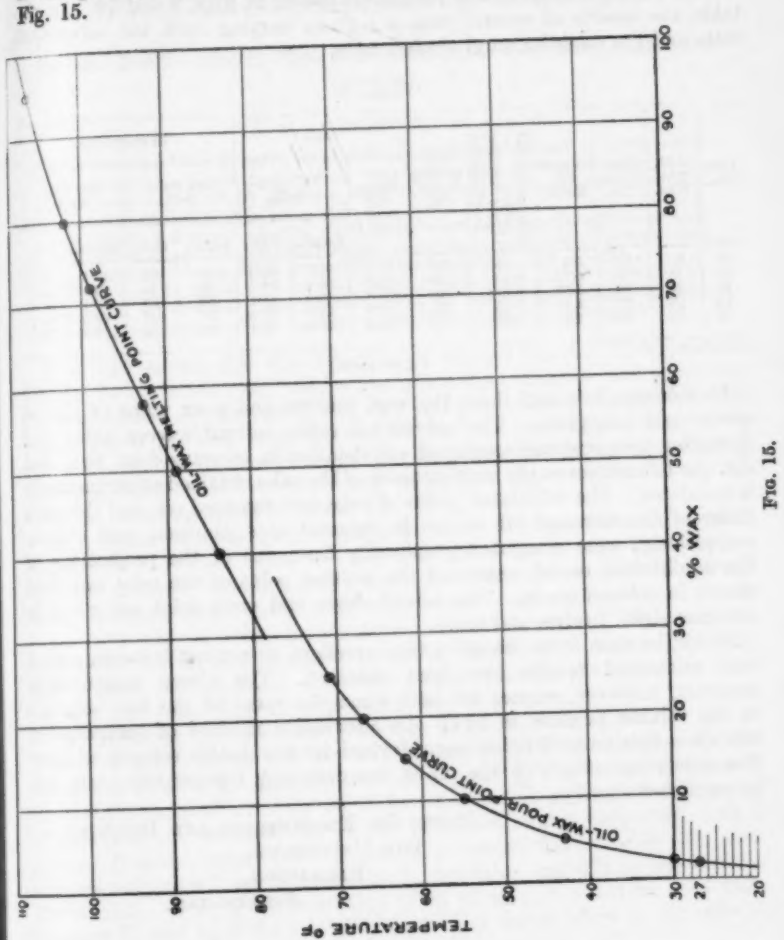


FIG. 15.

## COMPARISON OF CALCULATED AND EXPERIMENTAL DATA.

In order to check the accuracy of the computation methods, small-scale dewaxing operations were carried out using the same apparatus as that described in the previous paper [1] and following the same procedure. The experimental and calculated results are compared in Table I. The stock used was obtained by dissolving refined paraffin wax, melting point 108° F., in Anglo-Iranian second cooled blue oil. The two solvents employed were

light naphtha (b. pt. 100–120° C.) and amyl alcohol. All the dewaxing experiments were carried out at a temperature of 50° F. The equilibrium relationships in the system wax-oil–naphtha–amyl alcohol at 50° F. used for computing the calculated results are shown in Figs. 9 and 10. In the table the results of several runs are given varying both the solvent/oil ratio and the naphtha/amyl alcohol ratio.

TABLE I.

| Run No. | Per cent. Wax. | Pour Point, ° F. | Solvent/ Oil Ratio. | Solvent/solvent Ratio Light Naphtha : Amyl Alcohol | Dewaxing Temp., ° F. | Cake. | | | Dewaxed Oil. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Melting Point, ° F. | Per cent. Yield. | | Pour Point, ° F. | | Per cent. Yield. | |
| | | | | | | | Actual. | Calc. | Actual. | Calc. | Actual. | Calc. |
| 13 | 23 | 70 | 0·5 | 0·25 | 50 | 81 * | 45·7 | 45·6 | 53 | 54 | 54·1 | 54·4 |
| 14 | 23 | 70 | 0·75 | 0·25 | 50 | 86·3 | 36·6 | 36·7 | 54 | 55 | 63·4 | 63·3 |
| 15 | 23 | 70 | 1·07 | 0·071 | 50 | 79 * | 49·9 | 48·1 | 52 | 52 | 50·1 | 51·9 |
| 16 | 23 | 70 | 1·07 | 0·25 | 50 | 91·8 | 25·5 | 25·8 | 57 | 57 | 74·5 | 74·2 |
| 17 | 23 | 70 | 1·07 | 0·604 | 50 | 92·2 | 17·2 | 21·1 | 62 | 61 | 82·8 | 78·9 |

* Pour point.

In columns two and three the wax content and pour point of the oil stock used are given. The solvent/oil ratio, solvent/solvent ratio and dewaxing temperatures employed are detailed in columns four, five, and six. In column seven the melting point of the cake obtained experimentally is tabulated. The calculated yields of cake and dewaxed oil, and the pour point of the dewaxed oil, shown in columns nine, thirteen, and eleven, respectively, were computed graphically from one of the projections of the equilibrium model, assuming the melting point of the cake was that shown in column seven. The actual yields and pour point are given in columns eight, twelve, and ten.

It will be seen from the table that excellent agreement between actual and calculated results has been obtained. The above computation methods, however, cannot be used when the ratio of the two solvents in the solvent mixture is 1 : 1. An alternative method of computation free from this limitation has been devised for the double solvent mixture completely miscible with the oil at the dewaxing temperature, and will be published shortly.

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*Reference.*

[1] Ba Thi, Strang, Hunter, and Nash, *J.I.P.T.*, 1937, **23**, 226.

# DEWAXING WITH HEAVY SOLVENTS.*

By Dr. Bruno Engel (The Separator-Nobel Co., Ltd., Stockholm, Sweden).

SUMMARY.

It is shown that, by using a suitable specific heavy solvent or combination of solvents, distillates and residues originating from different crudes, which have been subjected to different treatments, can be successfully dewaxed by means of centrifuges.

Further, it is shown that, in some cases when treating oils rich in asphalt and resins, a partial precipitation and removal of such highly polymerized and condensed compounds is possible simultaneously with dewaxing.

The yield of oil, as well as the quality of the wax, can be improved by carrying out the dewaxing process in two or more stages, either by fractional precipitation of the wax, or by deoiling of the wax obtained.

It is well known that the dewaxing of mineral oils and their products has for its main purpose, besides the production of crude and pure wax, the preparation of lubricating oils with low pour points. In practice, the separation of the wax from the mother liquid is generally carried out at low temperatures by means of pressing, settling, filtering or centrifuging, after the addition of solvents which precipitate the waxes and keep the valuable oil components in solution.

As suitable solvents for this purpose, many different classes of organic compounds have been used, of which only those classes comprising hydrocarbons, alcohols, ketones, esters and their mixtures need be mentioned here. Besides these compounds, chlorinated hydrocarbons have lately come into use as wax precipitants and oil solvents. This may be attributed to their easy technical handling, which will be referred to later, and to their characteristic selectivity in precipitating the paraffinic components and dissolving the lubricating oil components.

The following considerations illustrate these characteristics:

It is of no importance if the wax is only slightly soluble in a certain solvent A at two different temperatures $t_1$ and $t_2$, where the difference in solubility compared with the oil to be separated is not sufficiently great. If, however, the wax and the oil can be mixed in any proportion with a solvent $B$ at a temperature $t_1$, and if a certain difference in solubility appears only at a lower temperature $t_2$, dewaxing can still be successfully carried out. If $L_1$ is the solubility of oil or wax in a solvent at a temperature $t_1$, and $L_2$ is the solubility at a lower temperature $t_2$, the solvent giving the highest value of $\frac{L_1 - L_2}{L_1}$ for the wax and simultaneously the lowest value for the oil will be the best one for dewaxing purposes.

This requirement is met by the chlorinated hydrocarbons of which the saturated chlorinated derivatives rank foremost. It has moreover been found that for homologous hydrocarbons with increasing chlorine sub-

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stitution, the wax solubility rises in much the same way as it falls at constant halogen content but with increasing hydrogen content, *i.e.* in the following order: substituted methanes, olefines, naphthenes, aromatics. In the case of evenly substituted chlorinated hydrocarbons, as far as the above-mentioned solubility characteristics are concerned, those which are symmetrically substituted are superior to the unsymmetrically substituted ones.

As a basic solvent for dewaxing with chlorinated hydrocarbons, dichlorethane has proved to be particularly suitable. This solvent has the following characteristics: specific gravity at 20° C. 1·26, specific heat at 30° C. 0·305, latent heat about 80, solubility for water 0·1 per cent. and boiling point 84° C. Trichlorethane is also excellent, but has a higher boiling point (114° C.) than dichlorethane. On the other hand, ethyl chloride, $C_2H_5Cl$, is not as suitable, its high vapour pressure (boiling point 13° C.) and low specific gravity, rendering it unsuitable for handling in settling-tanks and centrifuges.

It is well known that besides waxes and lubricants the oil products to be treated contain other components such as resins and asphalts, the molecular weight of which can vary within wide limits, depending on the boiling range and the degree of ageing of the raw material. These more or less harmful compounds have a detrimental effect on almost any known dewaxing process, not only because of their inhibiting effect on the crystallization of the wax, but also because they impair the mechanical separation. Filtration, for example, is particularly retarded by clogging of the filter pores.

In order to eliminate these harmful bodies, it is usual to introduce a refining process into the filtration which, without special precautions, results in excessively high losses of valuable lubricating components. These deleterious compounds are, of course, perceptible even when dewaxing with chlorinated hydrocarbons, although not in a detrimental way. Experience has shown that when dewaxing with these solvents, either a true solution or a precipitation of polymerized or condensed products can be obtained, depending on the nature of the oil to be dewaxed. In this way the last-mentioned products may either be divided among the components to be separated or removed together with the wax.

In order to illustrate the above, consider the dewaxing of the following two extreme products:

(1) A paraffin base oil.

(2) An asphalt base residue.

In the first case chilling in dichlorethane solution results only in a separation of the waxes, and an oil having a pour point below the dewaxing temperature may be obtained.

In the second case the asphalt bodies having the highest molecular weight are precipitated, besides the waxes, and on filtering or centrifuging, an oil having a pour point equal to the separating temperature may be obtained. Of course, when treating these oils rich in asphalts with the above-mentioned solvents, they are greatly conserved owing to the physical refining which takes place simultaneously with the dewaxing. If a subsequent refining should prove necessary, the corresponding losses will thus be reduced to a minimum.

The process is, of course, also suitable for the third group of oils, viz. the mixed base oils. These oils are characterized by their content of polymethylenes (naphthenes), polycyclic compounds, highly condensed products, etc. Since the constitution and molecular weights of these compounds vary within very wide limits, some, when treated with dichlorethane at a reduced temperature, may go into true solution, others may be precipitated, whilst still others may be colloidally dissolved or suspended.

In view of the well-known detrimental effect of colloidally dispersed components on any mechanical separating process, one has to employ remedies which will eliminate the colloidal character. This can be attained by means of auxiliary solvents, either by dissolving or by precipitating the above-mentioned compounds. As dissolving agents, benzol, toluol, xylol and other aromatic hydrocarbons, unsaturated hydrocarbons and their chlorine derivatives, *e.g.* trichlorethylene, may be used. As suitable precipitating agents may be mentioned ketones (such as acetone, methyl ethyl ketone, methyl *iso*butyl ketone), esters (such as methylformate, methylacetate and their homologues), alcohols etc.

Of the "solvents" mentioned above, the aromatic hydrocarbons, *e.g.* benzol, toluol etc., have the advantage of a relatively high value for the fraction $\frac{L_1 - L_2}{L_1}$. In many cases a combination of 75–78 per cent. dichlorethane and 25–22 per cent. benzol is used in practice in conjunction with centrifuges, whereby an easy separation of the light wax and the heavy mixture of oil and solvent is effected.

Another advantage to be considered in practice is the comparatively low degree of dilution and the moderate chilling required for precipitating the wax, when dichlorethane–benzol mixtures are used. Moreover, from an energy point of view, the process is inexpensive, since the specific heat (about 0·3 calories) and the latent heat (about 80 calories) of the solvent in question are lower than for many other solvents. The boiling points of the two solvent components dichlorethane (84° C.) and benzol (80° C.) are rather close to each other, which is of great importance in the recovery of the solvent. As already mentioned, dichlorethane has a solubility for water of about 0·1 per cent. at 20° C., from which a harmful effect on wax precipitation and danger of corrosion of dewaxing equipment might be feared. It has been found, however, that an azeotropic mixture of 9 parts of dichlorethane and 1 part of water can be distilled at 69° C. It is thus possible to obtain an almost complete dehydration. Furthermore, the decomposition of dry dichlorethane begins only at 165° C., a temperature far above the boiling point of the solvent.

The conditions for using the second group of auxiliary or additional solvents, especially the lower esters of formic and acetic acid and ketones which are resin and polymer precipitants, have proved to be equally favourable. The water solubility of the latter does not matter at all, since by adding dichlorethane a practically complete dehydration of the water-saturated esters or ketones can be obtained.

Depending on the requirements for the final products, one group or the other of auxiliary solvents, or a pure chlorinated hydrocarbon should be employed. According to the degree of the dissolving or precipitating

effect on the polymers, waxes of different quality may be obtained. It should be observed that if the polymers are removed together with the wax, the melting point of the latter is mostly reduced by the complex character of the polymers, since, as is well known, certain polymerized products act as pour-point reducers.

The following table shows the effect of dichlorethane and dichlorethane mixtures on polymerized products:

TABLE I.

*Content of Polymers.*

| Solvent | Nil | Medium | High |
|---|---|---|---|
| Dichlorethane | True solution | Colloidal solution | Non-reversible precipitation |
| Dichlorethane + dissolving agent | ,, ,, | True solution | Colloidal solution |
| Dichlorethane + precipitating agent | ,, ,, | Formation of flakes | Non-reversible precipitation |

The above table is, of course, only of a general nature, and it should be noticed that in many cases the oils to be treated are of a mixed nature and that the optimum dewaxing conditions are preferably determined by preliminary tests.

The polymerized compounds may be either of natural origin or formed during the pretreatment of the oil, particularly by pre-heating. That they influence the choice of the best solvents in each particular case, is proved by the fact that after their removal, *e.g.* by refining, the precipitating effect of the solvent is the same as when it is applied to a fresh resin-free distillate. Thus differences in quality between final products can be eliminated and the "spread" between the dewaxing temperature and pour point becomes the same in both cases.

This fact is of fundamental importance in dewaxing practice, since, as already mentioned, the centrifugal separation of wax from products rich in asphalt is greatly facilitated and filtration difficulties due to clogging of filter pores are eliminated.

Supposing that a complete separation of polymers with the wax is to be avoided, then the dewaxing of residues, rich in resins and asphalts, can be advantageously carried out by means of centrifuges, since the dissolving agents added partially transfer those bodies which impair separation, into the colloidal state, as shown in the table above, with the result that gravity settling would take place very slowly and filtration could be carried out only until filter pores became clogged. Consequently, centrifuges offer the only satisfactory means of separation. This is also confirmed by the fact that when dewaxing with mixtures of aromatics and ketones (*e.g.* benzol–acetone) the proportion of the former must be very large (although they are good wax solvents), in order to reduce the inhibiting and clogging effect of the resins. It is true that, owing to the high concentration of aromatics in such cases, a wax with a higher melting point is obtained, but the simultaneous increase of the yield of oil is largely due to the lower waxes being maintained in solution and hence impairing the pour point of the oil.

The proportion of solvents, such as benzol, to be added to dichlorethane, can be varied according to the quantity of polymers present in the oil.

This is particularly the case with aged and thermally pretreated oils, the resin contents of which may be such that an addition of up to 40 per cent. of benzol may be required. In centrifugal dewaxing there are certain limits for the addition of benzol, since the difference in specific gravity between the solvent and wax is reduced with an increased proportion of benzol. In such cases, dichlorethane can be replaced to a greater or smaller extent by the heavier trichlorethylene. Also mixtures of trichlorethylene with ketones or benzol as well as mixtures of dichlorethane with carbon tetrachloride can be used for obtaining the desired result.

By means of dichlorethane together with ketones, the polymers can be precipitated in a non-reversible state, the treatment thus being comparable with a physical refining process. This precipitation can also take place progressively and in several steps with decreasing temperature, whereby the separation of wax and resins takes place according to their molecular weight.

Also the dewaxing as such can be carried out to advantage in several stages, viz. in two alternative ways: (1) By fractional precipitation of wax at different temperatures and constant solvent proportion. (2) By fractional deoiling of wax by means of solvent distribution in separate stages.

The main advantage of this multi-stage process is the possibility of obtaining a maximum yield of oil with a minimum of solvent. Assuming for the sake of simplicity that the raw material is a wax from which lubricating oil should be extracted, the question is whether it is better to extract in one stage with a certain proportion of solvent, or to divide the solvent into two or more portions and carry out the process by means of corresponding separate extractions.

When treating a mixture of oil and wax with a solvent, the relation between the concentration of oil and that of wax in this solvent is the same as the relation between the solubility of oil and wax respectively in the solvent. If the solubility of oil in this solvent is twice as great as the solubility of wax in the solvent, two-thirds of the oil quantity ($A$) present in a certain volume of the raw material is extracted by an equal volume of solvent. In other words, with one part by volume of solvent a quantity of oil corresponding to $0{\cdot}67A$ is extracted.

If, on the other hand, the extraction is carried out in two stages, each with half the above-mentioned volume of solvent, the oil quantity $X$ is extracted in the first stage, leaving $A - X$ in the wax. The relation between the concentrations of oil is then $(A - X) : \frac{X}{0{\cdot}5} = \frac{A - X}{2X}$. Thus: $\frac{A - X}{2X} = \frac{1}{2}$ or $X = 0{\cdot}5A$. At the second extraction with the second half of the solvent quantity, half of the oil still contained in the wax is extracted from it, *i.e.* $0{\cdot}25A$. In total, $0{\cdot}75A$ may thus be extracted in the two stages, *i.e.* a larger proportion than when carrying out the process in only one stage. By using a still greater number of stages, the yield of oil can be further increased. For practical reasons, however, the number of stages is limited.

Besides ensuring a higher yield, the multi-stage process has the advantage of giving under certain conditions a better quality of oil, the selectivity

of the above-mentioned solvents ensuring also a lower wax concentration when using a reduced quantity of solvent. This is shown in the following table, based on dewaxing an Alsacian distillate by means of dichlorethane.

TABLE II.

| Number of Stages. | Temperature, ° C. | Solvent, % by vol. | Total Yield, %. | Pour Point of Oil, ° C. |
|---|---|---|---|---|
| 1 | −10 | 1 × 300 | 67·0 | −18 |
| 2 | −10 | 2 × 150 | 71·5 | −19 |
| 1 | −20 | 1 × 300 | 59·0 | −24 |
| 2 | −20 | 2 × 150 | 65·6 | −28 |

The proportions of solvent to be used in the first and the second stage, respectively, can of course be varied in relation to each other, with due regard to technical considerations in centrifuging. It should be noted that the primary wax always contains a certain proportion of solvent, and that the additional quantity of solvent required for the second treatment can thus be reduced. According to experience, the first stage should always be carried out with the smallest possible quantity of solvent, since a more satisfactory pour point for the primary oil can then be obtained by moderate chilling. The following figures are of interest in this respect when dewaxing in two stages:

TABLE III.

| Number of Stages. | Temperature, ° C. | Total Quantity of Solvent, % by vol. | Yield of Oil, %. | Pour Point of Oil, ° C. |
|---|---|---|---|---|
| 1 | −31 | 450 | 87·2 | − 9 |
| 2 | −31 | | | |
| 1 | −24 | 350 | 75·1 | −20 |
| 2 | −21 | | | |

These figures prove that it is possible to obtain a better pour point with less solvent and with less chilling than under reversed conditions, but only at the expense of a certain reduction in yield, which can be limited, however, by modifying the operating conditions, *e.g.* by introducing a third stage of treatment.

When using chlorinated hydrocarbons as solvents for multi-stage dewaxing, it is not necessary to re-dissolve the wax after each stage and then chill the wax again. This is an advantage of the chlorinated hydrocarbons over most other solvents.

In certain cases, *e.g.* when treating oils very rich in wax, it may be just as advantageous to carry out a fractional *precipitation* of the wax. This is done by first chilling the solution of oil rather moderately, thus precipitating the hardest waxes. These are then removed by centrifuging and the centrifuged oil solution is further chilled and centrifuged again. Also, when working in this way much less solvent is required than when working in one stage. Moreover, waxes of different qualities (as far as melting points are concerned), can be obtained. It goes without saying that in regard to the wax obtained, fractional wax-precipitation can be combined with fractional wax-deoiling.

The question of chilling conditions is of particular importance during dewaxing. The rate of chilling and flow conditions prevailing in the liquid during chilling, the effect of under-chilling, thixotropy, and redissolving, owing to fine dispersion of precipitated particles, etc., play an important part. Moreover, the influence of the colloidally precipitated and/or redissolved resins and asphalts on the crystallization and solubility of the waxes must be considered. It is thus obvious that the optimum conditions for obtaining the best possible yield and qualities can only be determined empirically.

The necessary chilling time, from room temperature to −10 or −20° C., varies from ½ to 2½ hours, depending on the content of higher polymers as well as on the wax content of the oil. When centrifuging, the viscosity of the mixture is also of importance, and it is well known that the viscosity of a liquid containing a certain amount of solids is lower the less colloidal is the degree of dispersion. Reduced viscosity facilitates the precipitation and results in a higher yield, owing to smaller quantities of occluded oil. In order to ensure a good crystallization of wax out of oils free from resins but rich in wax, it is often of advantage to increase the time of chilling up to the above-mentioned upper limit of about 2½ hours.

Experience has shown that when using less dilution, the time of chilling may be reduced, which is also the case if a mixture of dichlorethane and benzol is used instead of pure dichlorethane. Moreover, the chilling should be carried out as evenly as possible and with a medium degree of agitation, so as to ensure a partly laminar and partly turbulent flow of the liquid.

The following figures show some typical examples of the effect of the above-mentioned solvents and their combinations on oils of various origin and character. For the sake of simplicity, the multi-stage processes are not taken into consideration, and moreover the same operating conditions have been assumed in each case, so as to permit a direct comparison.

*Abbreviations:* S. = Solvent, *e.g.* benzol, toluol, trichlorethylene.
P. = Precipitant, *e.g.* ketones, esters, etc.

TABLE IV.

*Light Midcontinent Distillate.*

Characteristics: Specific gravity 0·873 at 15° C.
Viscosity 2·47° E. at 38° C.
Pour point + 17° C.

| Solvent. | Additional Solvent. | Dilution, % by vol. | Temperature, ° C. | Yield of Oil, %. | Pour Point, ° C. |
|---|---|---|---|---|---|
| Dichlorethane | — | 300 | − 5 | 92·4 | − 6 |
| do. | S. | 300 | − 5 | 93·0 | + 5 |
| do. | — | 300 | −20 | 82·0 | −23 |
| do. | S. | 300 | −20 | 86·8 | −20 |
| do. | P. | 300 | −20 | 86·0 | −31 |
| do. | — | 100 | −20 | 74·0 | −27 |
| do. | P. | 100 | −20 | 73·0 | −32 |
| do. | — | 500 | −20 | 87·0 | −25 |
| Trichlorethane | — | 300 | −20 | 86·6 | −19 |
| do. | P. | 300 | −20 | 77·0 | −32 |
| Gasoline | — | 300 | −20 | 73·0 | − 6 |
| do. | P. | 300 | −20 | 81·5 | −17 |

The above figures show that the yields as well as the pour points can be varied in any desired direction, simply by varying the composition of the solvent, the temperature and the degree of dilution. Also the influence of increasing chlorine substitutes (dichlorethane, trichlorethane) is shown. The selective properties of the chlorinated hydrocarbons as compared with gasoline can be clearly seen. The additional solvents (S. and P.) represent as a maximum 25 per cent. of the total volume of solvent, and the superiority of the chlorinated hydrocarbon combinations over the pure hydrocarbons such as gasoline, is rather striking.* It will also be seen that aero-engine oils with pour points far below the dewaxing temperature can be produced with moderate chilling in the presence of precipitants.

In Table V a comparison is made between some of the solvents described in Table IV when used for dewaxing heavier and more waxy distillates. In view of the higher wax content, a larger degree of dilution was used.

TABLE V.

*Lobitos Distillate.*

Characteristics: Specific gravity 0·906.
Viscosity 1·96° E. at 99° C.
Pour point 53·5° C.

| Solvent. | Additional Solvent. | Dilution, % by vol. | Temperature, ° C. | Yield of Oil, %. | Pour Point, ° C. |
|---|---|---|---|---|---|
| Dichlorethane . . | — | 400 | — 3 | 47·0 | —13 |
| do. . . | — | 400 | —15 | 42·5 | —17 |
| do. . . | S. | 400 | —15 | 46·0 | —10 |
| do. . . | P. | 400 | —10 | 42·0 | —22 |

*Alsacian Distillate.*

Characteristics: Specific gravity 0·932.
Viscosity 11·8° E. at 50° C.
Pour point + 34° C.

| | | | | | |
|---|---|---|---|---|---|
| Dichlorethane . . | — | 300 | —10 | 65·6 | —17 |
| do. . . | P. | 300 | —10 | 67·0 | —18 |
| do. . . | P. | 300 | —20 | 59·0 | —24 |
| do. . . | S. | 300 | —20 | 62·0 | —20 |

As will be seen, a low pour point can be obtained with moderate chilling. The spread between chilling temperature and pour point is reduced with decreasing dewaxing temperatures. The presence of precipitants results in a considerable lowering of the pour point without essentially impairing the yield. This fact is not surprising, since it could be proved that by adding 1–3 per cent. medium or soft wax to an oil with low pour point, the latter can be increased by 10° C. or more.

Table VI shows the figures obtained with a heavy Roumanian distillate which has been subjected to a long time of storage and thus represents an intermediate product between fresh distillate and residue.

Already in this case the presence of ageing and decomposition products obstructs to some extent the precipitating effect as will be seen from the

* The wax-precipitating action of dichlorethane is so specific that it could probably be utilized in wax analyses.

smaller "spread." At low temperatures the difference between precipitants and dissolving agents becomes smaller and smaller.

TABLE VI.

*Roumanian Distillate.*

Characteristics: Specific gravity 0·912.
Viscosity 2·37° E. at 99° C.
Pour point 55° C.

| Solvent. | Additional Solvent. | Dilution, % by vol. | Temperature, ° C. | Yield of Oil, %. | Pour Point, ° C. |
|---|---|---|---|---|---|
| Dichlorethane . . | — | 400 | −10 | 34·0 | −10 |
| do. . . | P. | 400 | −10 | 42·0 | −16 |
| do. . . | P. | 400 | −20 | 39·2 | −21 |
| do. . . | S. | 400 | −20 | 39·0 | −21 |

The nature of the wax crystals which can be observed in the microscope under polarized light must, of course, be considered, particularly when comparing yields. Depending on the liquid from which the waxes are precipitated, different crystal structures are obtained which in their turn determine the quantity of occluded oil and thus also the yield obtainable.

In the case of certain distillates rich in resins, the spread between the dewaxing temperature and the pour point can be reversed in the presence of precipitants. In other words, at a higher temperature $t_1$ a pour point below $t_1$ can be obtained, whereas at a lower temperature $t_2$ the pour point may be higher than $t_2$. This is due to the simultaneous "refining" or removal of certain polymers which takes place at the lower temperature, such bodies acting as pour point reducers (wax inhibitors).

The resin and asphalt precipitating effect is, of course, particularly striking in the case of residues, as shown in Table VII representing the distribution of individual groups of polymers in the products. The raw material was in this case a topped Roumanian oil.

TABLE VII.

| Raw Material, % by Weight. | | Lubricating Oil Phase. | | Wax Phase. | | In Wax Phase, Calculated on 100% Raw Material. |
|---|---|---|---|---|---|---|
| | | Weight. | % | Weight. | % | |
| Asphalts . . . | 0·3 | 0·0 | 0·0 | 0·3 | 0·5 | 100 |
| Resins, soluble in pyridine . . | 7·4 | 2·4 | 6·3 | 5·0 | 8·1 | 67·5 |
| Resins, soluble in chloroform . . | 7·3 | 3·0 | 7·9 | 4·3 | 7·1 | 59·0 |
| Wax . . . | 37·0 | 1·7 | 4·5 | 36·2 | 58·2 | 96·0 |
| Oil . . . . | 47·1 | 30·9 | 81·3 | 16·2 | 26·1 | 34·4 |
| | 100·0 | 38·0 | 100·0 | 62·0 | 100·0 | |

According to this table, dichlorethane has a similar, although not as strong a refining action as the lower hydrocarbons such as butane, pentane, etc. The influence on the viscosity and the V.I. of the final products is analogous, in so far as the viscosity increases and the V.I. decreases with increasing concentration of complex polymers.

Table VIII shows the figures obtained with a highly asphaltic residue. It will be seen that in such cases dissolving agents should preferably be added, and that an increased concentration of these (*e.g.* trichlorethylene) can be of advantage:

TABLE VIII.

*Oklahoma City, Long Residue.*

Characteristics: Specific gravity 0·930.
Viscosity 4·45° E. at 99° C.
Pour point + 28° C.

| Solvent. | Additional Solvent. | Dilution, % by vol. | Temperature, ° C. | Yield of Oil, %. | Pour Point, ° C. |
|---|---|---|---|---|---|
| Dichlorethane . . | — | 300 | −20 | 56·0 | −10 |
| do. . . | S. | 300 | −20 | 86·0 | −19 |
| Trichlorethylene . . | — | 300 | −20 | 50·0 | −11 |
| do. . . | P. | 300 | −20 | 88·0 | −17 |

Whereas in the above tables mainly the effect of the solvents and their various combinations have been shown, the following table IX indicates under which operating conditions it is possible to obtain a final product with a certain pour point, when using the various solvent combinations.

TABLE IX.

*Iraq Light Distillate.*

Characteristics: Specific gravity 0·895.
Viscosity 2·03° E. at 50° C.
Pour point + 26·5° C.
Pour point desired: −20° C.

| Solvent. | Additional Solvent. | Dilution Required. | Temperature Required, ° C. | Yield of Oil Obtainable in One Stage, %. |
|---|---|---|---|---|
| Dichlorethane . | — | 200 | −16 | 77·2 |
| Trichlorethylene . | — | 175 | −35 | 76·0 |
| Dichlorethane . | P. | 200 | −14 | 78·0 |
| do. . | S. | 200 | −19 | 80·0 |
| Trichlorethylene . | P. | 175 | −25 | 78·5 |

*Iraq Heavy Distillate.*

Characteristics: Specific gravity 0·926.
Viscosity 11·7° E. at 50° C.
Pour point +35° C.
Pour point desired: −20° C.

| | | | | |
|---|---|---|---|---|
| Dichlorethane . | — | 200 | −17 | 58·8 |
| Trichlorethylene . | — | 180 | −32 | 60·0 |
| Dichlorethane . | P. | 200 | −20 | 62·7 |
| do. . | S. | 180 | −20 | 58·1 |
| Trichlorethylene . | P. | 200 | −24 | 62·0 |

*Iraq Cylinder Oil.*

Characteristics: Specific gravity 0·951.
Viscosity 32° E. at 50° C.
Pour point +32° C.
Pour point desired: −20° C.

| | | | | |
|---|---|---|---|---|
| Trichlorethylene . | P. | 200 | −26 | 80·0 |
| Dichlorethane . | P. | 200 | −23 | 67·0 |
| do. . | S. | 200 | −20 | 72·0 |

By selecting a suitable solvent, the pour point desired in each case can be obtained without difficulty with the types of oil mentioned above. It is true that, when using other dilutions, other temperatures must be selected. The above figures of dilution and temperature are the optimum ones, however, which can easily be determined for each particular type of raw material.

Depending on whether a removal of polymers simultaneously with dewaxing is desired, and with due regard to the requirements not only of the lubricating oil, but also of the wax, dichlorethane and trichlorethylene may be used alone or in combination with dissolving or precipitating agents. If the dewaxing does not take place until after a previous refining, the use of dichlorethane alone or in the presence of precipitants is generally of advantage, since the differences against the polymer-free distillates are then eliminated. When treating long cuts, dichlorethane alone should generally be preferred, and in the case of aged products or residues, a certain addition of solvents such as hydro-aromatics, aromatics or unsaturated compounds is preferable.

Since dichlorethane has a comparatively high specific gravity (1·26), the above-mentioned examples and figures can be applied also to centrifugal separation, the use of which is rapidly extending. For instance, the well-known Separator-Nobel or Barisol process has lately been greatly improved from a chemical as well as a centrifugal point of view.

It has been shown how the yield of dewaxed oil can be increased by using two- or multi-stage treatment for fractional precipitation or deoiling of wax. These processes are of special practical importance because the removal of only small quantities of wax can result in a considerable reduction in pour point. A corresponding increase in yield can also be obtained in a similar way by adding small quantities of synthetic lubricating oil obtainable in the market as pour-point reducers. The latter process which is protected by Messrs. I.G. Farbenindustrie and the Standard Oil Co. can be applied with advantage to centrifugal dewaxing by the S–N or Barisol process using the solvents mentioned above.

Whereas, the synthetic oils merely reduce the pour point of the oil to which they are added, their addition prior to dewaxing with chlorinated hydrocarbons results simultaneously in an increase in yield, the extent of which depends on the quantity of polymers present in the oil. On the other hand, when it is the question of obtaining a certain pour point, the addition of the synthetic oil permits the dewaxing to be carried out at a considerably higher temperature, and thus a material saving in refrigerating costs is obtained. This effect is rather remarkable seeing that the presence of pour-point reducers when dewaxing with many other solvents generally improves *either* the yield *or* the pour point, whereas in the present case the results are improved in *both* these respects.

It is obvious that the solvents and their combinations described above can be used not only for dewaxing of lubricating oils and their fractions, but also for deoiling of petrolatum, purification of crude wax, etc. While it is not the place to go into such details here, it may suffice to mention that the results obtained in the laboratory could always be satisfactorily reproduced in practice under similar operating conditions.

# THE INFLUENCE OF CERTAIN SUBSTANCES ON THE SEPARATION OF PARAFFIN WAX FROM OIL IN A DEWAXING PROCESS.*

By E. C. H. Kolvoort, F. R. Moser and C. G. Verver.

Synopsis.

When waxy crude oils are distilled, a point is generally reached when subsequent (higher boiling) fractions contain a type of paraffin wax of very poor crystalline character, having a bad filterability and showing a high oil retention. This point occurs at a very much lower stage in the distillation with some crudes than with others. The authors believe that the phenomenon may be explained by the occurrence of branched-chain paraffins together with those of normal type.

The counteraction of oil adsorption to such kinds of waxes by the aid of "wax conditioners" or "dopes" ("pour-point depressants") is discussed and a hypothesis explaining the observed phenomena is developed.

## A. Substances Promoting the Retention of Oil by Wax.

It is a well-known fact that various types of waxy crude oils differ in the character of the paraffin wax present in the heavier distillates. On the one hand, we have the "classical" base materials for the manufacture of commercial paraffin wax, such as some of the Borneo, Java and Rangoon oils. Many of these may be distilled almost (though not quite) as far as modern equipment will permit, and will then yield overhead fractions containing a highly crystalline wax, which may be filtered off without difficulty and without the use of diluents. The majority of waxy oils, however, are not as tractable as these. It will, for instance, be frequently observed that on distilling a certain raw material only the fractions up to, say, the spindle (and perhaps the light engine) oil contain paraffin wax of a good crystalline character; the higher fractions are often not only unfilterable as such, but when added to the light fractions may completely spoil their filterability.

In the days before the advent of selective dewaxing solvents, this property considerably limited the production of lubricating oils from the second type of base materials. Now that good diluents (for instance, ketone–benzol mixtures) are available, the untractable higher fractions may also be dewaxed. Even then, however, it will be found that the wax cakes obtained hold considerable amounts of oil very tenaciously. In solvent dewaxing it is by no means unusual to meet with cakes containing 30 per cent. or more of oil, and obviously this tendency greatly diminishes the yields of dewaxed lubricating oils in the plant, besides spoiling the quality of the wax cakes themselves.

In view of the practical importance of the problem, some comparative dewaxing experiments have been carried out by the authors on cuts obtained in an analogous manner from a number of waxy crude oils, and some attempts have been made to explain the observed differences.

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Although further work is in progress, it is believed that certain conclusions can already be reached from the results obtained.

Distillation was carried out on residues obtained from the various crudes in a special vacuum still, provided with a 6-foot column packed with rings and with a mechanical reflux return; the reflux ratio was kept at 10 : 1 during distillation. Preliminary experiments had shown that this arrangement gave a very satisfactory fractionation, even in the higher ranges. Fractions of approximately 3 per cent. were collected. A number of these—sufficient to give the desired course of the properties studied—were subsequently solvent-dewaxed under certain standard conditions, similar to those met with in practice, viz. :

Solvent, methyl ethyl ketone–benzol 50/50 parts by volume; dilution ratio, 1 : 3 by vol.; chilling temperature, — 27° C.; average chilling rate, 2° C. per min.; filtration on chilled suction funnels (13 cm. diameter) through a single layer of cloth; wash ratio, 1 : 1 by vol. calculated on waxy oil (temperature — 27° C.).

A number of characteristic properties were determined on the original 3 per cent. fractions and on the wax cakes and filtered oils obtained, including specific gravities at 70° C., viscosities, molecular weights * and melting points of the wax cakes. In order not to present too many figures,

TABLE I.

*Properties of Original Fractions, Waxes and Dewaxed Oils from Java Crude Oil.*

| Fraction No. | % by wt. on res. | Fraction. | | Dewaxing. | | Oil. | | | Wax Cake. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $d^{70}_4$. | M. pt., ° C. | Oil % (wt.). | Cake % (wt.). | $d^{70}_4$. | $V_S$/ 50° C. (c.st.). | Mol. wt. | $d^{70}_4$. | Mol. wt. | M. pt., ° C. |
| 1 | 3·17 | 0·8492 | — | 70 | 29 | 0·8961 | 5·9 | — | 0·7552 | — | 33 |
| 2 | 3·19 | 0·8460 | — | 66 | 34 | 0·9035 | 9·2 | 270 | 0·7585 | 293 | 38 |
| 3 | 3·13 | — | — | — | — | — | — | — | — | — | — |
| 4 | 3·01 | 0·8392 | 29½ | 59 | 41 | 0·9046 | 11·1 | — | 0·7620 | — | 43 |
| 5 | 3·03 | — | 33 | — | — | — | — | — | — | — | — |
| 6 | 2·96 | — | 35½ | — | — | — | — | — | — | — | — |
| 7 | 3·33 | 0·8321 | 38 | 49 | 50 | 0·9060 | 19·4 | 329 | 0·7678 | 328 | 49½ |
| 8 | 2·68 | — | 40½ | — | — | — | — | — | — | — | — |
| 9 | 2·68 | — | 40 | — | — | — | — | — | — | — | — |
| 10 | 2·98 | 0·8410 | 42 | 53 | 47 | 0·9212 | 31·8 | — | 0·7705 | — | 52½ |
| 11 | 2·77 | — | 44½ | — | — | — | — | — | — | — | — |
| 12 | 3·15 | — | 46 | — | — | — | — | — | — | — | — |
| 13 | 2·88 | 0·8364 | 48 | 48 | 52 | 0·9214 | 55·4 | 370 | 0·7743 | 387 | 58 |
| 14 | 3·08 | — | 50½ | — | — | — | — | — | — | — | — |
| 15 | 3·40 | — | 51 | — | — | — | — | — | — | — | — |
| 16 | 3·17 | 0·8422 | 51½ | 46 | 53 | 0·9273 | 106·9 | — | 0·7784 | — | 61 |
| 17 | 3·60 | — | 52½ | — | — | — | — | — | — | — | — |
| 18 | 3·18 | — | 54 | — | — | — | — | — | — | — | — |
| 19 | 2·58 | 0·8406 | 55 | 45 | 55 | 0·9332 | 181·0 | 411 | 0·7794 | 434 | 63½ |
| 20 | 3·07 | — | 57 | — | — | — | — | — | — | — | — |
| 21 | 2·78 | 0·8505 | 58 | — | — | — | — | — | — | — | — |
| 22 | 2·91 | 0·8523 | 58½ | 48 | 51 | 0·9356 | 212·0 | — | 0·7845 | — | 67 |
| 23 | 2·80 | — | 59 | 50 | 50 | 0·9353 | 216·0 | 449 | 0·7872 | 490 | 67 |
| 24 | 2·95 | 0·8579 | 59½ | 48 | 51 | 0·9349 | 222·0 | — | 0·7933 | — | 67½ |
| 25 | 3·25 | — | 60 | 53 | 47 | 0·9409 | 306·0 | — | 0·7974 | — | 67 |
| 26 | 3·06 | 0·8803 | 58 | 52 | 47 | 0·9506 | 497·0 | 465 | 0·8090 | 527 | 66 |

* Determined cryoscopically in naphthalene solution.

the data for the two extreme cases only will be given here, viz. for a waxy Java crude and a Roumanian paraffin base oil. These are typical examples of the two types of waxy oils referred to in the opening paragraph, in the order cited. The figures obtained are collected in Tables I and IA.

TABLE IA.

*Properties of Original Fractions, Waxes and Dewaxed Oils from Roumanian Crude Oil.*

| Fraction No. | % by wt. on res. | Fraction. | | Dewaxing. | | Oil. | | | Wax Cake. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $d_4^{70}$. | M. pt., ° C. | Oil % (wt.). | Cake % (wt.). | $d_4^{70}$. | $V_3$/ 50° C. (c.st.). | Mol. wt. | $d_4^{70}$. | Mol. wt. | M. pt., ° C. |
| 1 | 2·9 | 0·8060 | — | 78 | 21 | 0·8217 | 3·56 | — | 0·7539 | 279 | 27 |
| 2 | 3·08 | — | — | — | — | — | — | — | — | — | — |
| 3 | 2·82 | 0·8198 | — | 73 | 26 | 0·8454 | 4·97 | — | 0·7577 | — | 32 |
| 4 | 2·96 | — | — | — | — | — | — | — | — | — | — |
| 5 | 3·17 | 0·8245 | 23½ | 68 | 32 | 0·8573 | 6·76 | 295 | 0·7623 | 319 | 43 |
| 6 | 3·10 | — | 29½ | — | — | — | — | — | — | — | — |
| 7 | 2·91 | 0·8302 | 29½ | 67 | 33 | 0·8624 | 11·7 | — | 0·7688 | 357 | 48 |
| 8 | 3·17 | — | 33 | — | — | — | — | — | — | — | — |
| 9 | 2·32 | 0·8353 | 35 | — | — | — | — | — | — | — | — |
| 10 | 2·63 | — | 37 | 67 | 32 | 0·8733 | 22·1 | 367 | 0·7738 | 393 | 54 |
| 11 | 2·92 | 0·8429 | 39½ | — | — | — | — | — | — | — | — |
| 12 | 2·90 | — | 41 | — | — | — | — | — | — | — | — |
| 13 | 2·77 | 0·8504 | 43 | 67 | 31 | 0·8858 | 42·6 | 390 | 0·7803 | 411 | 57½ |
| 14 | 3·15 | — | 43 | — | — | — | — | — | — | — | — |
| 15 | 2·79 | 0·8572 | 44 | — | — | — | — | — | — | — | — |
| 16 | 2·84 | 0·8602 | 45 | 70 | 28 | 0·8950 | 72·6 | — | 0·7890 | — | 58 |
| 17 | 3·10 | 0·8614 | 46 | 66 | 30 | 0·8944 | 83·8 | 417 | 0·7933 | 435 | 61 |
| 18 | 3·03 | 0·8624 | 47½ | 65 | 33 | 0·8939 | 95·6 | 455 | 0·8042 | 460 | 61 |
| 19 | 3·27 | 0·8639 | 49 | 57 | 41 | 0·8953 | 120·0 | — | 0·8232 | — | 61 |
| 20 | 2·36 | 0·8650 | 52 | 58 | 41 | 0·8949 | 131·8 | — | 0·8246 | 507 | 62 |
| 21 | 3·11 | 0·8708 | 54 | 53 | 45 | 0·9032 | 200·6 | 508 | 0·8365 | 550 | 62 |
| 22 | 3·43 | 0·8748 | 56½ | 44 | 53 | 0·9093 | 300·0 | — | 0·8479 | — | 63 |
| 23 | 1·92 | 0·8787 | 57 | 35 | 61 | 0·9151 | 407·0 | — | 0·8593 | 580 | 64 |

In the graph given in Fig. 1, the specific gravities at 70° C. of the waxes have been plotted against their molecular weights. The graph includes the specific gravities at 70° C. of the normal paraffin series, calculated from data given in the literature; a smooth curve was drawn through the plotted points, which show some spreading. (As the normal paraffins above 450 mol. wt. have melting points above 70° C., the upper part of the curve has been shown as a dotted line.)

It may be remarked in this connection that the specific gravities of branched-chain ("*iso-*") paraffins, up to a molecular weight of about 400, differ but little from those of their normal isomers; above 400 the *iso*-paraffins tend to have a somewhat higher specific gravity. The melting point–mol. wt. curve for the *n*-paraffins is also shown in the graph. The melting points of the *iso*-paraffins are, of course, considerably lower than those of their normal isomers.

It will be observed that the Roumanian and Java fractions show a marked difference in accordance with their behaviour in practice. Both follow the curve for the pure *n*-hydrocarbons closely up to a certain point, and then rise upwards somewhat sharply. The departure from the curve

is due to the retention of oil in the wax. The point of departure, however, is about 100 points in mol. wt. *lower* in the case of the Roumanian material than in that of the Java fractions, *i.e.* the Java waxes tend to hold but

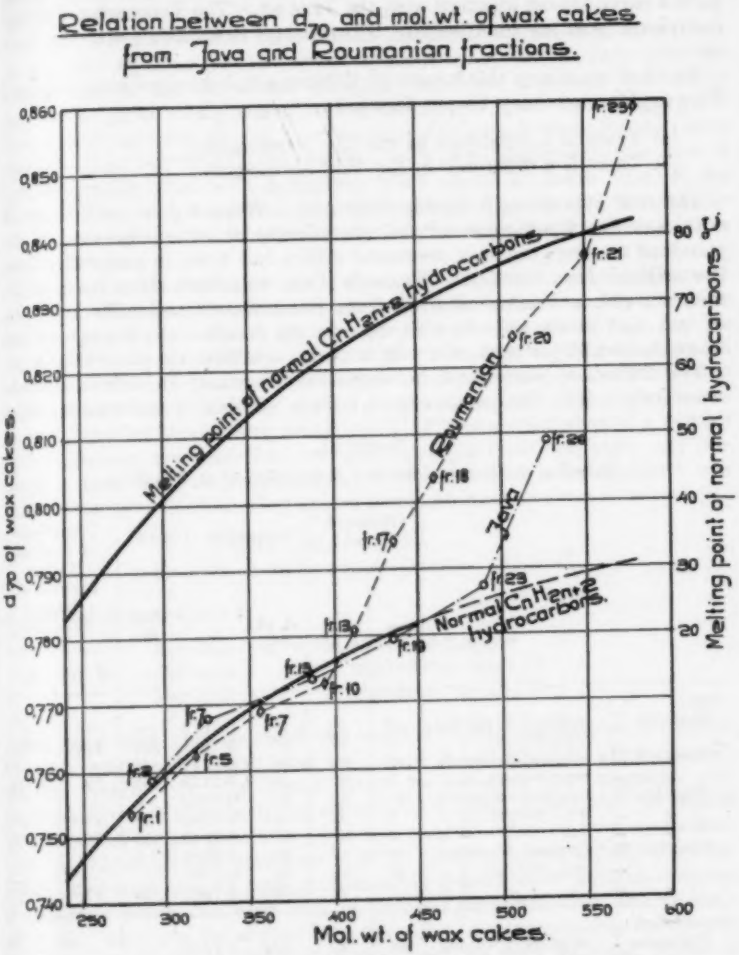


FIG. 1.

little oil over the mol. wt. range 390–490, whilst the Roumanian fractions do so to a considerable extent.

It should be noted that this range is a very important one (although fairly short on the graph): it covers a considerable part of the components in commercial waxes, whilst a mol. wt. of 390 (in the Roumanian example)

corresponds approximately to the border-line between the spindle oil and the heavier lubricating distillates.

(Two other base materials have been examined in the same manner, *i.e.* a Borneo waxy oil and a Venezuelan paraffin base stock. The former gave a curve almost identical with the Java oil. The Venezuelan material occupies a position intermediate between the Roumanian and the Java oil.)

To what cause may this important difference in behaviour be attributed? Two explanations may be put forward:

(*a*) There is a difference in the oily components;
(*b*) There is a difference in the solid components.

The first hypothesis is readily disproved. When a Java wax is mixed with wax-free Roumanian oil and the mixture is solvent-dewaxed in the standard manner, the wax recovered differs but little in properties from the original Java fraction. (Example: the wax from Java fraction 23, mol. wt. 490, was mixed with oil from Roumanian fraction 19—mol. wt. of wax also about 490—in a 50 : 50 ratio by weight. On dewaxing there was obtained 53 per cent. of a cake with $d_{70} = 0{\cdot}7904$, m. pt. = 66½° C.)

The difference must hence be sought in the wax. In order to obtain some insight into this peculiarity, a certain number of the wax fractions

TABLE II.

*De-oiling of Certain Java and Roumanian Wax Fractions.*

| | Obtained (% wt.). | | Properties of Wax. | | | Properties of Normal Hydrocarbons of Same Mol. Wt. | |
|---|---|---|---|---|---|---|---|
| | Oil. | Wax. | M. pt., ° C. | $d_{70}$. | Mol. Wt. | M. pt. | $d_{70}$. |
| *Java*: | | | | | | | |
| Fraction 7: original dewaxing | 49 | 50 | 49½ | 0·7678 | — | — | — |
| „ „ wax recryst. 1 × | 2 | 97 | 50 | 0·7661 | 334 | 49½ | 0·767 |
| Fraction 13: original dewaxing | 48 | 52 | 58 | 0·7743 | — | — | — |
| „ „ wax recryst. 1 × | 3 | 96 | 59 | 0·7728 | 380 | 59 | 0·774 |
| Fraction 23: original dewaxing | 47 | 52 | 66 | 0·7900 | — | — | — |
| „ „ wax recryst. 1 × | 8 | 92 | 66½ | 0·7853 | — | — | — |
| „ „ „ „ 2 × | 2 | 97 | 67 | 0·7848 | 490 | 75 | 0·785 |
| Fraction 26: original dewaxing | 52 | 47 | 66 | 0·8090 | — | — | — |
| „ „ wax recryst. 1 × | 10 | 90 | 66 | 0·7997 | — | — | — |
| „ „ „ „ 2 × | 2 | 98 | 66½ | 0·7990 | 516 | 77 | 0·787 |
| *Roumanian*: | | | | | | | |
| Fraction 5: original dewaxing | 66 | 32 | 42½ | 0·7620 | — | — | — |
| „ „ wax recryst. 1 × | 2 | 97 | 42½ | 0·7613 | 310 | 43½ | 0·762 |
| Fraction 13: original dewaxing | 67 | 31 | 57 | 0·7797 | — | — | — |
| „ „ wax recryst. 1 × | 2 | 98 | 58½ | 0·7771 | 405 | 63½ | 0·777 |
| Fraction 23: original dewaxing | 39 | 58 | 64 | 0·8545 | — | — | — |
| „ „ wax recryst. 1 × | 37 | 62 | 65 | 0·8320 | — | — | — |
| „ „ „ „ 2 × | 10 | 89 | 67 | 0·8141 | — | — | — |
| „ „ „ „ 3 × | 5 | 95 | 68 | 0·8113 | — | — | — |
| „ „ „ „ 4 × | 2 | 97 | 68½ | 0·8095 | 574 | 81½ | 0·790 |

were further de-oiled by recrystallization from methyl ethyl ketone-benzol 50/50, 1 : 10 at — 27° C. (wash : 1 : 1). The de-oiling was carried out partly on fresh batches of wax, which hence differ slightly in properties from those given in Table I. The following results were obtained (see Table II).

It will be observed from these results that the fractions, in so far as they lie near the $d_{70}$-lines for the normal hydrocarbons, contain very little oil. In the case of the Java base material, the lower fractions are readily purified to yield waxes which correspond closely, both in melting point and specific gravity, to the normal straight-chain hydrocarbons. Java fraction 23 on recrystallization yields a wax of approximately the correct specific gravity, but with a melting point about 8° below that of the corresponding *n*-hydrocarbon. In the case of fraction 26, the specific gravity remains about 0·012 point too high, whilst the melting point is 12° too low.

The Roumanian fraction 5 would also appear to consist largely of normal paraffins. Fraction 13, after one recrystallization, yields a product which has the specific gravity of the straight-chain hydrocarbons, but has an appreciably inferior melting point. The primary wax from fraction 23 contains at least 50 per cent. of oil, and it will be seen that this is retained with extraordinary tenacity during recrystallization. After the fourth recrystallization the melting point is still 13° lower than that of a normal hydrocarbon of the same mol. wt. and the $d_{70}$ is 0·010 too high. At this stage a ring analysis according to Waterman and collaborators [1] was carried out, and the following figures were obtained :

$d_4^{70} = 0{\cdot}8095$; $n_D^{70} = 1{\cdot}4520$.
Mol. wt. = 574; aniline point = 131·6° C.

Derived ring analysis :

Per cent. carbon in aromatic rings, 0
Per cent. „ „ naphthenic rings, 0.
Per cent. „ „ paraffinic chains, 100.

We have been able to check the method of ring analysis on a number of pure paraffin hydrocarbons, and have found that it gives entirely reliable results; it may hence safely be assumed that aromatic and naphthenic rings are absent in all but very small quantities. It should be mentioned in this connection that the material removed by recrystallization in M.E.K.–benzol 50/50 at — 27° C. is in all cases an oil, liquid at 0° C.; although this oil may contain small quantities of solid substances, it generally differs but very little in physical properties from the primary filter oil. It might be argued that the substances responsible for the oil-retaining properties of the higher wax fractions may be small traces of non-paraffins (*e.g.* ring compounds) which are removed during recrystallization. This is disproved by the following evidence :

(*a*) Drastic treatment with earth, sulphuric acid or fuming acid of the original wax does not alter its oil-retaining properties (*i.e.* aromatic bodies are not responsible).

(*b*) When the four times recrystallized Roumanian fraction No. 23

was mixed with its *primary* filter oil in the calculated proportion (50 : 50 by wt.), and the mixture was again recrystallized, it was found that it exhibited the same tenacious retention of oil, the course of recrystallization being almost identical with that of the original wax from fraction 23. The following results should be compared with those given in Table II:

| | | | | | | |
|---|---|---|---|---|---|---|
| First recrystallization; | oil 38%; | wax 62% | (m. pt. 65½°, | $d_{70}$ = 0·8293). |
| Second | „ | ; „ 12%; | „ 88% | ( „ 67½°, | „ = 0·8130). |
| Third | „ | ; „ 5%; | „ 94% | ( „ 68½°, | „ = 0·8110). |
| Fourth | „ | ; „ 2%; | „ 98% | ( „ 68½°, | „ = 0·8085). |

The authors believe that from the evidence given above they may assume that the peculiar oil-retaining qualities of the higher Roumanian wax fractions (and probably of other similar cases) must be explained mainly by the presence of branched-chain paraffin hydrocarbons. The occurrence of *iso*-paraffins in certain wax fractions has been suggested by several investigators [2, 3, 4, 5]; on the other hand, various authors believe that solid hydrocarbons containing cyclic nuclei may also be present. [6, 7, 8] The present authors have found no evidence of the presence of solid cyclic hydrocarbons in the wax fractions examined by them, and although they may occur in other types of wax, it is apparent that the branched-chain paraffins are sufficient to explain the "abnormal" tendency to oil retention of certain wax fractions. It is also not impossible that the presence of cyclic compounds in certain relatively small wax fractions prepared by certain investigators may be due to traces of oil; the above results demonstrate the extraordinary difficulty of eliminating the last traces of fluid hydrocarbons when dealing with a wax of "oil-retaining" type.

The authors consider that it is very desirable for information to be collected in this field (as in all others connected with the properties of the higher petroleum fractions) by synthesizing pure hydrocarbons and studying their effect on one another. A commencement in this direction has been made in the Laboratory of the Bataafsche Petroleum Maatschappij.

### B. Substances Counteracting the Adsorption of Oil on Wax.

Certain types of wax thus appear to have a remarkable tendency to adsorb oil, a fact which in commercial dewaxing results in lower lubricating oil yields and wax cakes of high oil content. Various attempts in the authors' laboratory to *destroy* the promotors of this oil-adsorption, viz. the branched-chain paraffins, by various means (*e.g.* selective cracking, various chemical treatments) have so far met with very little success.

Fortunately there are means of counteracting this tendency to oil retention, although they are seldom able to overcome it entirely. This is by the use of those substances known as "wax conditioners" (or "dewaxing dopes"). The action of these bodies probably has the same cause as that of the well-known "pour-point depressants" (such as "Paraflow" [9]); in fact, in the authors' laboratory the two terms have for some time been regarded as synonymous, a particular substance being always suitable for both purposes.[10]

The addition of such a substance to a waxy oil may result in three effects of technical importance:

A. The pour point of the original (waxy) oil may be lowered.

B. The amount of oil retained by the cake when the oil is dewaxed (either as such or in a solvent) may be lowered.

C. The speed of filtration in dewaxing may be increased.

It should be noted that effect A (and, of course, effect B) occur only in those cases when the wax is of that type which tends to retain oil. An explanation of these phenomena will be put forward later.

For the sake of convenience we may classify the various "wax conditioners" and "pour-point depressants" in the following entirely arbitrary (and unscientific) manner:

Group i. Synthetically produced organic chemicals of more or less definite structure, including "Paraflow" (a Friedel-Crafts condensation product of naphthalene and chlorinated paraffin wax) and compounds such as octastearyl-saccharose,[11] rufigallic acid hexastearate,[12] etc.

Group ii. Dark-coloured bodies of undefined structure, pyrogenically formed in the process of cracking a hydrocarbon or fatty oil.

Group iii. Soaps of polyvalent metals.

The substances in group i, although possibly of great interest as "pour-point depressants," are, generally speaking, too costly to be considered as "dewaxing dopes," and will therefore not be further dealt with here.

Group ii is probably at present the most interesting from a technical point of view. When certain hydrocarbon oils are submitted to a cracking operation, it will be found that the cracked residue may have developed the desired active properties to a marked degree. A considerable amount of experimental work has been done by the authors on such pyrogenically formed bodies, and some of the results may be summarized here as follows:

(*a*) The active properties are concentrated in those fractions precipitated by solvents such as aromatic-free 60/80 spirit, pentane, etc., *i.e.* in the so-called "asphaltenes."[10, 13]

(*b*) These "asphaltenes" are formed from aromatic hydrocarbons. (A medicinal oil gives practically no active bodies on cracking, an aromatic extract a very high yield of them.[10])

(*c*) Only "asphaltenes" pyrogenically formed in the cracking reaction are effective. ("Asphaltenes" precipitated from an uncracked crude oil or residue are inactive.)

(*d*) The efficiency of the asphaltenes is to a large extent a problem of colloid-chemical nature. Fluid cracked residues gradually lose their potency as "dewaxing dopes" owing to coagulation of the active bodies. Such deteriorated "dopes" may be regenerated by heating, either alone or with peptizing agents. Reheating to temperatures below commencement of cracking also frequently enhances the activity of a fresh cracked residue.[10, 14] The efficiency further depends on the manner (especially the temperature) of solution of the "dope" in the oil, diluted oil or solvent.

Group ii may be taken to include certain types of fatty acid pitches, many of which are highly active. The "pyrogenic" group has one disadvantage: although the active bodies are precipitated on (and removed with) the wax, cracked residues always contain dark-coloured, *inactive*

substances which colour the filtrate. The discoloration is generally not removable by clay, but very readily by a slight acid treatment.

Among the soaps in group iii the most important is aluminium stearate, although a few other active soaps (*e.g.* ferric stearate and titanium stearate) have been found. It is a remarkable fact that no soaps derived from a high molecular acid other than the saturated fatty acids (stearic and palmitic), such as oleic, ricinolic, lauric and various naphthenic acids, have as yet been found to show any activity whatsoever. In general, it may be stated that practically nothing is known with regard to the factors determining the activity of a soap (or any other type of compound, for that matter) as a "dewaxing dope," and many unexplained phenomena are met with, and may still be expected.

It has been found that a combination of a "pyrogenic" dope with aluminium stearate shows a particularly high activity.

In order to illustrate the influence exerted by "dewaxing dopes," the following parallel results obtained on a distillate from a waxy Venezuelan oil may be given. The dewaxing experiments were in all cases carried out in cooled suction funnels, employing benzol–methyl ethyl ketone 50/50 (vol.) as diluent, a dilution ratio of 1 : 3 (vol.) on oil, a dewaxing temperature of — 20° C., and a proportion of cooled wash solvent of 1 1 (on original oil). 100 g. of oil were used for each experiment; the filtration times are those for 100 and 200 ml. of total filtrate.

TABLE III.

*Action of Various "Dopes" on the Dewaxing of a Venezuelan Waxy Distillate.*

| | Yields (% wt.). | | Filtration Times. | | "Filtration Factor" (*b*) | Pour-Point Filter Oil (*c*) | M. pt. of Wax Cake, ° C. |
|---|---|---|---|---|---|---|---|
| | Oil. | Wax Cake. | 100 ml. | 200 ml. | | | |
| No "dope" . . . | 56·5 | 43·5 | 1′ 9″ | 4′ 34″ | — | —13° | 47° |
| 0·5% of pyrogenically formed "dope" . . | 65·0 | 35·0 | 34″ | 1′ 50″ | 2·3 | —13° | 48° |
| 1% of pyrogenically formed "dope" . . | 68·0 | 32·0 | 21″ | 1′ 3″ | 3·8 | —13° | 49° |
| 0·1% of Al-stearate . | 76·0 | 24·0 | 14″ | 46″ | 5·4 | —13° | 50° |
| 0·1% of Al-stearate and 0·5% of pyrogenic "dope" . . . | 79·0 | 21·0 | 10″ | 28″ | 8·4 | —13° | 52° |

(*b*) Average factor for filtration speed improvement over 100 and 200 ml. of filtrate.
(*c*) After earth treatment.

Whilst much remains to be solved with regard to the action of "pour-point depressants" or "dewaxing dopes," the following explanation has proved to be very useful as a working hypothesis. This may be regarded as an extension of the explanation given by Zimmer, Davis and Frolich.[15]

It is believed that the bodies are substances of polar character possessing a particular affinity for the surface of a crystal of paraffin wax. If a solution of wax crystallizes out in the *absence* of such an active body, a considerable number of crystal nuclei are formed, each of which "grows up" to an individual crystal (Fig. 2). If now the wax is of the "oil-

retaining " type, oil is adsorbed on the wax. For the sake of simplicity it may be considered that each crystal carries a " shell " of oil, as shown in the figure. When the particles are in sufficient proximity, interlocking (" gelling ") will occur, and the oil shows a relatively high pour point. It is also plausible that such " solvatized " wax will filter less readily than a system containing free crystals suspended in oil.

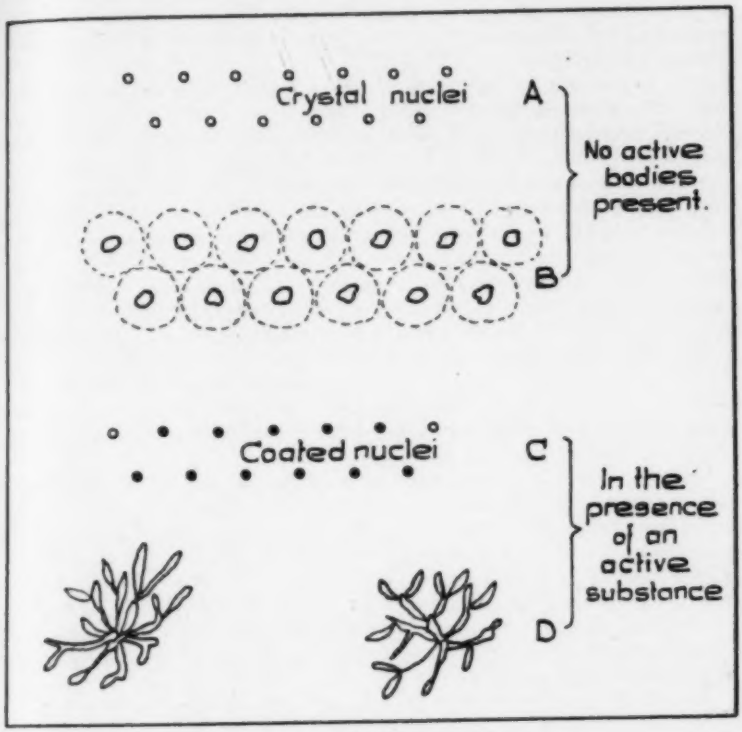


FIG. 2.

CRYSTALLIZATION OF AN " OIL-RETAINING " PARAFFIN WAX IN THE ABSENCE AND IN THE PRESENCE OF AN ACTIVE SUBSTANCE.

In the presence of a suitable active body, the greater part of the wax nuclei will be coated with this active substance immediately on formation, and crystallization will take place on only a few nuclei which have escaped this action, or where a " weak spot " occurs. The result is in general the formation of a few relatively large crystal aggregates; the appearance of the crystal aggregates may vary somewhat with the type of " dope " added. As these crystals develop, the coating of active substance on their surface is continually maintained and extended; the characteristic formation of a feathery aggregate may be explained by assuming that it

is frequently easier for a crystal to continue its growth at a " weak spot " in the coating than to develop in its original shape.

The active body thus adsorbed on the wax surface, if of suitable structure, exerts a repellent action towards oil. It is removed with the wax on filtration. If there is a surplus of active material, this will pass into the filtrate and act as a " pour-point depressant " in the filter oil. If too little is present, it will be used up during the first stages of wax crystallization, and crystallization will proceed during the later stages as though no active substance were present (*i.e.* fresh crystal nuclei will be formed and individual crystals will develop).

This hypothesis readily explains why a " pour-point depressant " has little or no action on the pour point of certain waxy distillates. The main cause of the pour-point depression is probably the " loosening " of adsorbed oil. A mere alteration in the type of crystallization (*e.g.* the formation of aggregates) may also have an effect, but probably not nearly so marked a one. Hence distillates containing wax of a " non-retaining " type will be affected but little, if at all. Effects A and B mentioned on pp. 740–741 are of practical interest only if the wax is of the " oil-retaining " type; effect C may theoretically also occur with " non-retaining " waxes (since aggregates may filter more readily than small individual crystals), but the practical effect is in general small in such cases.

It is clear that these active substances should have no influence on the *amount* of pure wax present in a solid crystalline form at a definite temperature, and dilatometric measurements show that this is actually the case. Nor is the temperature at which crystallization commences (*i.e.* the cloud point) noticeably affected.

Some photographs are appended to show the influence of an active body on the microscopic appearance of the image. They were taken in an apparatus permitting of a very accurate temperature control of the sample examined. In all cases a solution of a narrow distillate cut of a Borneo wax (m. pt. 49·7° C.), consisting almost entirely of normal paraffin hydrocarbons, in a medicinal oil (viscosity : 30·3 c.st./100° F.; $d_{25} = 0{\cdot}8723$), was employed, the concentration being such (about 20 per cent.) that crystallization commenced at approximately 30° C., on employing a rate of cooling of 5° C. per hour.

Fig. 3*a* shows crystallization in the absence of an active substance.

Fig. 3*b* illustrates the influence of a very minute trace (0·009 per cent.) of aluminium stearate. There is a definite reduction in the number of crystals, whilst an increased tendency to the formation of aggregates may be observed.

Fig. 3*c* shows the very marked reduction of nuclei and the occurrence of aggregate formation on adding more (0·04 per cent.) aluminium stearate; the exposure was made at 29·65° C.

Fig. 3*d* is of the same preparation at a slightly lower temperature (28·85°). (The whole aggregate shown had developed from a single nucleus.)

Fig. 3*e* and *f* similarly illustrate the appearance at two successive temperatures (29·2° and 27·9° C.) when still more aluminium stearate is added (0·078 per cent.). Crystallization here commences only at the very edge of the solution, all further nuclei being suppressed.

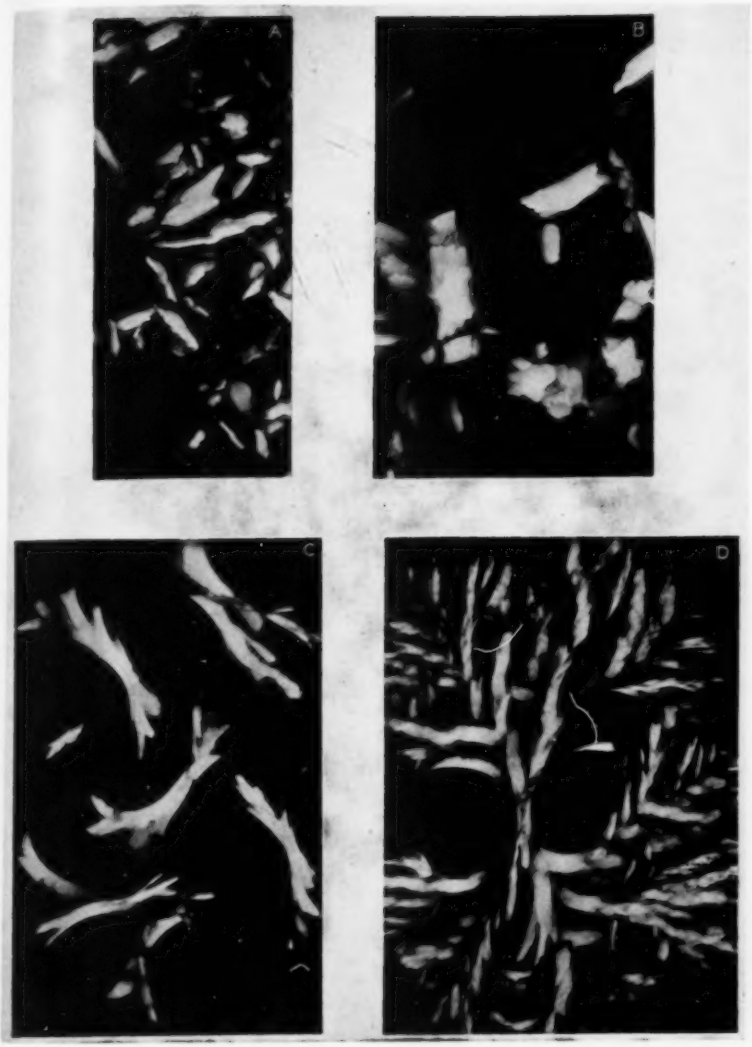


FIG. 3.

CRYSTALLIZATION OF A SOLUTION OF A BORNEO PARAFFIN WAX FRACTION IN MEDICINAL OIL.

(Photomicrographs between crossed nicols, 37 ×.)

A. No active substance added.
B. + 0·009% aluminium stearate.
C. + 0·04% aluminium stearate (29·65° C.).
D. + 0·04% aluminium stearate (28·85° C.).

[*To face p.* 744.

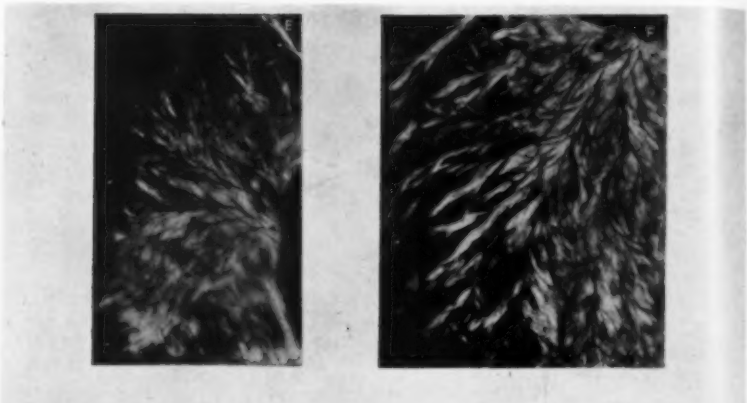

FIG. 3 (*cont.*).

CRYSTALLIZATION OF A SOLUTION OF A BORNEO PARAFFIN WAX FRACTION IN MEDICINAL OIL.

(Photomicrographs between crossed nicols, 31 ×.)

E. + 0·078% aluminium stearate (29·2° C.).
F. + 0·078% aluminium stearate (27·9° C.).
G. + 0·65% aluminium stearate.
H. + "pyrogenic dope."
I. + "pyrogenic dope."

Fig. 3*g* shows the results of a very large quantity of aluminium stearate (0·65 per cent.).

Fig. 3*h* and *i* demonstrate that the action of a pyrogenically formed "dope" (a cracked aromatic extract) results in a very similar effect to that of aluminium stearate.

In conclusion, it may be stated that the adventitious presence of active bodies of this nature is a point which needs careful watching in all dewaxing experiments. Luboil distillates may contain traces of "natural" dopes as a result of slight cracking or entrainment during distillation. The removal of a high-boiling solvent, if done carelessly, may introduce a "pour-point depressant" after dewaxing. It is hence desirable in comparative laboratory work to give the material an earth treatment (which completely removes all active bodies) both before and after dewaxing.

Certain references in literature can be readily explained by the presence of such active bodies. A striking example is that of the "lubricating oils showing the phenomena of high and low pour point" of Moore and Beard,[16] who give photomicrographs clearly showing aggregate formation.

The authors wish to thank the Bataafsche Petroleum Maatschappij for permission to publish these results.

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[15] Zimmer, Davis and Frolich, *Penns. State Coll. Bull.*, 1933, **12**, 57; *J.I.P.T.*, 1934, Abstr. 555.
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# METHYL NORMAL-BUTYL KETONE AS A DEWAXING SOLVENT.*

By O. S. Pokorny and R. K. Stratford.

Before deciding whether or not a solvent (or solvent mixture) may be used commercially in a dewaxing process, its behaviour should be studied from the following points of view :

(1) Solubility of wax in the solvent.
(2) Miscibility temperature of oil and solvent.
(3) Rate of filtration.
(4) Difference between dewaxing and pour temperatures.
(5) Recovery of the solvent.
(6) Stability and corrosive characteristics of the solvent at high temperatures.
(7) Inflammability of the solvent.
(8) Toxicity of the solvent.
(9) Cost of the solvent.

In the following paragraphs the behaviour of methyl *n*-butyl ketone will be discussed under the above headings.

## (1) Solubility of Wax in the Solvent.

Fig. 1 shows the solubility of 141–143° F. melting-point paraffin wax in a number of dewaxing solvents, including methyl *n*-butyl ketone. As may be seen from the graph, the solubility of this wax in methyl *n*-butyl ketone is comparatively low, so that this ketone should act as an excellent precipitant for paraffin wax. Because of the low solubility, a comparatively high dewaxing temperature may be employed to obtain a given pour point.

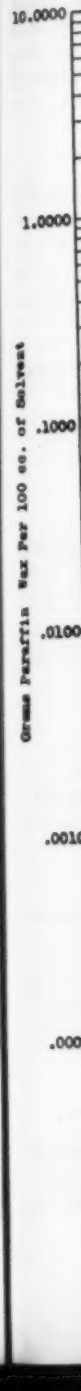
## (2) Miscibility Temperature of Oil and Solvent.

The miscibility temperature of a sample of phenol treated dewaxed Mid-Continent heavy distillate having a viscosity of 125 S.U. at 210° was determined when diluted with two volumes of ketone. This oil was chosen because a solvent-extracted heavy distillate would be expected to have a high miscibility temperature, whilst a dilution of 2 : 1 is in the range employed for solvent dewaxing. The miscibility point for various ketones is shown in the following table :

*Miscibility Temperature of Phenol Treated Heavy Mid-Continent Distillate Dilution* 2 : 1.

| Ketone. | Miscibility Temp. ° F. |
|---|---|
| Methyl Ethyl Ketone | + 78 |
| Methyl *n*-Propyl Ketone | + 11 |
| Methyl *iso*-Butyl Ketone | − 14 |
| Methyl *n*-Butyl Ketone | − 38 |
| 50% Methyl Ethyl Ketone / 50% Benzol | − 9 |

* Paper presented for Discussion at the One Hundred and Seventy-seventh General Meeting of the Institution of Petroleum Technologists, November 9th, 1937.



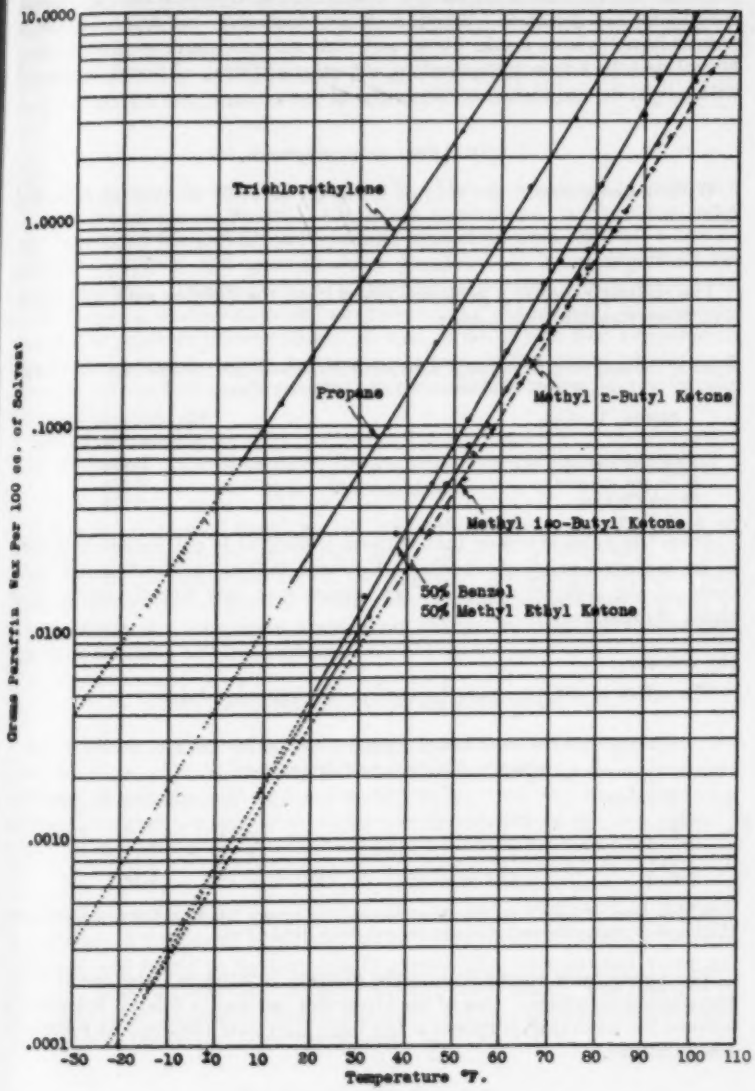



FIG. 1.

SOLUBILITY OF 141–143° F. M.P. PARAFFIN WAX IN VARIOUS SOLVENTS.

Of the four ketones listed, methyl *n*-butyl ketone is seen to have the lowest miscibility temperature. When used for dewaxing, no separation of a second liquid phase would occur with this solvent above — 38°, so that benzol or toluol is not required to obtain miscibility, although necessary with a light ketone such as methyl ethyl ketone.

### (3) Rate of Filtration.

With a given stock, the rate of filtration depends on chilling rate and dilution.

(a) *Chilling Rate.*

The chilling rate has a profound effect upon the filtering rate, as may be seen from the following table:

*Effect of Chilling Rate on Solution throughput Mid-Continent Paraffin Slop* 70/75 *S.U. at* 210° F. *Dilution* 1·5 : 1. *Filtering Temp.* 15° F.

| Chilling Method. | Imperial Gallons of Solution/Sq. Ft./Hr. |
|---|---|
| 1° F. per minute | 0·371 |
| 3° F. per minute | 0·204 |
| Shock Chilling | 0·175 |

From this table it is seen that uniform chilling of 1° per minute is greatly to be preferred to shock chilling. Uniform chilling, in itself, is not sufficient, as the uniform rate of 3° per minute was only slightly better than shock chilling.

(b) *Dilution.*

The effect of dilution may be seen in the following table:

*Filtering Mid-Continent Heavy Paraffin Distillate* 240/250 *S.U. at* 100° F. *Methyl* n-*Butyl Ketone Filtering at* 12° F.

| Dilution. | Imp. Gals./Sq. Ft./Hr.* |
|---|---|
| 1·25 : 1 | 3·75 |
| 1·5 : 1 | 4·21 |
| 1·75 : 1 | 4·79 |
| 2·0 : 1 | 5·42 |

* This rate is based on filtration through a rotary vacuum filter, for constant thickness of wax cake and washing for constant yield of oil.

The above table shows that as the dilution is increased, the dewaxed oil throughput increases. One of the attractive features of *n*-butyl ketone as a solvent for dewaxing purposes is the high filter rate obtained at relatively low dilutions.

### (4) Difference between Dewaxing and Pour Temperatures.

A number of experiments on Mid-Continent distillates has shown that the dewaxed oil has a pour point in many cases lower than the dewaxing temperature. This is in line with the data presented in Graph No. 1, which

showed that the solubility of 141–143° F. m.p. wax at dewaxing temperatures was extremely low. The fact that a comparatively high dewaxing temperature may be employed to obtain a given cold test is of considerable importance from both the installation and operation points of view, as it indicates that a minimum of refrigeration will be required.

### (5) Recovery of the Solvent.

Methyl *n*-butyl ketone boils at 258° F. This temperature is such that either atmospheric or vacuum distillation methods of recovery (or both) may be applied without difficulty, whilst separation from the oil is a simple matter. At 77° F. 100 parts of water dissolve only 0·42 part of methyl *n*-butyl ketone. This solubility is low enough to permit a limited amount of steam stripping without entailing too great a loss. At ordinary temperature the vapour pressure is low enough (10 mm. at 68° F.), so that evaporation losses will be slight. From lengthy experience in the use of phenol as a selective solvent, it is believed that the overall ketone loss in a dewaxing plant will be very low.

### (6) Stability and Corrosive Characteristics of the Solvent at High Temperatures.

A sample of methyl butyl ketone was refluxed in a closed system at atmospheric pressure for fifty hours in the presence of test-pieces of steel plate, one in the liquid and one in the vapour. No sign of decomposition could be detected; no gas was formed, the solvent changed only slightly in colour, while the test-pieces showed no change in weight. The ketone therefore is stable and non-corrosive.

### (7) Inflammability of the Solvent.

The explosion limits of methyl *n*-butyl ketone are 1·2 to 8 per cent. by volume in air. The closed cup flash is 60° F. Excepting the chlorinated solvents, this flash point is considerably higher than the usual dewaxing solvents, making the solvent a comparatively safe one to use in a plant.

### (8) Toxicity of the Solvent.

A concentration of 0·1 per cent. was found by the U.S. Bureau of Mines Experimental Station at Pittsburgh to be irritating to the eyes and nose of man but was found to be harmless to guinea pigs after several hours exposure. This concentration is below the explosive limit. The presence of solvent vapour is therefore readily detectable before reaching concentrations dangerous to the health or safety of men.

### (9) Cost of the Solvent.

Methyl *n*-butyl ketone is produced by Stanco Inc. from secondary hexyl alcohol, itself a derivative of petroleum. It sells at about 15c. per pound. In cost, it is thus comparable with phenol which has been used successfully as a selective solvent in the petroleum industry for seven years.

## Conclusions.

From the view-point of wax solubility, miscibility temperature with oil, filter rates and cold test-dewaxing temperature relationship, methyl *n*-butyl ketone behaves in an excellent manner. Its vapour pressure is such as to render recovery a comparatively simple matter without entailing large evaporation losses. It is stable and non-corrosive under distillation conditions; it is non-toxic, and, due to its characteristic smell, its presence can be noted long before the concentration reaches the lower explosive limit, making it a safe solvent. The cost of the solvent is reasonable, and in the price range of selective solvents already successfully employed by the industry. This solvent should find wide application for dewaxing purposes.

# DISCUSSION ON DEWAXING.

THE One Hundred and Seventy-seventh General Meeting of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, W.C., on Tuesday, November 9th, 1937, at 5.30 p.m.

The President, Lieutenant-Colonel S. J. M. AULD, O.B.E., M.C., D.Sc., occupied the Chair, and the following papers were presented :—

"The Principles of Solvent Dewaxing. Part II: Equilibria and Computations for Double Solvent Systems." By M. Ba Thi, B.Sc., A.I.C. (Student Member), T. G. Hunter, Ph.D., A.R.T.C., A.I.C. (Member), and A. W. Nash, M.Sc., M.I.Chem.E., M.I.Mech.E. (Member). (*See* p. 707.)

"Dewaxing with Heavy Solvents." By Dr. Bruno Engel (The Separator-Nobel Co., Ltd., Stockholm, Sweden). (*See* p. 723.)

"The Influence of Certain Substances on the Separation of Paraffin Wax from Oil in a Dewaxing Process." By E. C. H. Kolvoort, F. R. Moser and C. G. Verver. (*See* p. 734.)

"Methyl Normal-Butyl Ketone as a Dewaxing Solvent." By O. S. Pokorny and R. K. Stratford. (*See* p. 746.)

In the absence of Dr. Hunter through illness, Mr. M. BA THI read a short summary, prepared by Dr. Hunter, of the four papers, and showed a number of lantern slides.

## *DISCUSSION.*

MR. C. G. VERVER said that in any dewaxing process the cardinal feature to be considered was, of course, how much good oil of a low pour point could be obtained from any particular waxy stock. The paper which he had prepared, in collaboration with Mr. Kolvoort and Mr. Moser, dealt with one particularly unpleasant feature which was found when certain types of wax were dealt with, *i.e.* the extraordinary tendency which some waxes showed to retain oil. The paper had therefore been divided into two parts, the first part dealing with the fact that certain waxes did retain oil and the reason why that was so, and the second part being an answer to the question as to what could be done about it.

He and his collaborators had in their laboratory fractionated a number of waxy crude oils into narrow cuts; a number of these fractions had been dewaxed in a standard manner, and the waxes and filter oil which had been obtained had been closely examined. This examination had shown that there were very considerable differences between the waxes occurring in different types of crude oils, and, from various experiments, which were described in the paper, he and his collaborators had concluded that the substances which caused the difference between the various waxes occurring in the different types of oil were branched-chain paraffin hydrocarbons.

The second part of the paper dealt with one method of partly overcoming the oil retention difficulty, *i.e.*, by means of dewaxing dopes, which were referred to in America as wax conditioners. Those substances were very probably identical with certain materials which had been known for a long time and were used to a very great extent in commercial work—namely, pour-point depressors, of which Paraflow was the first representative. These substances were probably compounds having a very high affinity for the surface of a wax crystal. When waxy oil crystallized out in the absence of one of those substances, a large number of nuclei were formed, each of which grew up to a crystal of a certain size. If those crystals were of that type of wax which had a tendency to retain oil, they might be regarded as being surrounded by a shell of oil, and the result would be interlocking at a certain point and the oil would gell at a comparatively elevated temperature, and have a high pour point. When an active substance was added before crystallization took place, nuclei were formed in the same way, but, owing to the high affinity of such substances (which were probably of more or less polar character) for the surface of the wax, a great many of the nuclei were, so to speak, nipped in the bud and could not grow any further. The wax, of course, had to come out somewhere, and it chose the weakest links in the chain and came out at one or two nuclei only. The peculiar feature observed was that those crystals very often developed into feathery aggregates. That was probably due to the fact that, as the crystals increased in size, the coating of active substance was maintained, and it was very often more easy for a crystal to bud out again at another spot than to extend indefinitely along its three axes. The active substance itself was oil-repellent, so the coating of oil would be smaller than it would be when the active substance was not used. Moreover, it was obvious that a few large groups of crystals floating about in an oil would have less tendency to interlock than a mass of small, "oil-coated" crystals would have, and that explained the pour-point reducing effect. The second effect, which was of very great technical importance, was that the filtration speed in the dewaxing process was immensely increased—sometimes ten times—by the use of a proper dope. The third effect, which followed immediately, was that the amount of oil adsorbed by the wax cake could be very considerably reduced.

The President (Lt.-Colonel S. J. M. Auld) said he would like to have some light thrown upon the dewaxing temperature differentials. He noticed that Messrs. Pokorny and Stratford, for example, directed special attention in their paper to the results that they had obtained with methyl *n*-butyl ketone, by stating that the dewaxed oil had in many cases a pour point lower than the dewaxing temperature itself. That, of course, implied that such a result was not usually the case, nor did he believe it to be so, although he was naturally open to correction. On the other hand, Dr. Engel in his paper quoted case after case in which dichlorethane mixtures, more particularly when given a double stage treatment, produced oils having a pour point very appreciably lower than the temperature of operation. He thought it was fully realized that the solubility of the wax in the solvent itself must have a predominating influence on this effect, but it was quite clear that that was not the only cause. Dr.

Engel's results showed appreciable differences between crude oils in that respect, although most of them gave products lower in pour point than the temperature of operation. Presumably the effect might be directed by the nature of the wax and its adsorbability for the oil, as explained by Messrs. Kolvoort, Moser and Verver, but he would like to know whether that was the case.

It appeared from the paper by Messrs. Ba Thi, Hunter and Nash that the pour point of an oil might be forecast by their three-dimensional graphical methods, using a knowledge of the melting point of the solvent-free cake. Their results were laboratory results obtained by using refined wax dissolved in blue oil, and he would much like to know from the authors whether their methods could be applied to the conditions described, for example, by Messrs. Kolvoort, Moser and Verver—in other words, would the intractable Roumanian oils give similar results to those given by the Java or Burma oils, or would it be necessary to introduce a fresh factor in the method of calculation in order to make the method applicable in practice in forecasting refinery conditions?

The second point which he would like to have elucidated for his own benefit was with regard to the partition of the wax-conditioning agents or the dewaxing "dopes" between the oil and the wax. There was no specific statement in the paper by Mr. Verver and his colleagues that the conditioning agent was removed with the wax, but he thought it was implied, by reference to the effect of the coloured pyrogenic dopes on the cake, that they appeared in the wax and were not retained by the oil subsequently. He thought also that that could be confirmed by other results elsewhere. He would like to deduce from that something which might not be strictly deducible, but, at any rate, was of some interest, *i.e.*, that any corresponding materials originally present in the crude oil and having similar effects would also be removed in the precipitated wax. In the paper by Mr. Verver and his colleagues reference was made only to the pyrogenic residues and materials actually formed by cracking, but he thought it was quite likely that similar materials were normally present in the crude oils. If that were the case, was the filterability of the wax any measure of the presence or of the removal with that wax of materials which might otherwise be of certain lubricating value to the oil itself?

He mentioned that because, although it was another assumption to make, it was of some significance that the type of compounds that had been mentioned, especially in Class 2, were somewhat of the same general nature as those that had been described elsewhere, particularly by Rosen, as having a marked anti-ring sticking effect in certain high-speed Diesel engines. It was possible that another cause of "over-refining" crude oil lay therein. In other words, that the removal of wax might also be responsible, as well as the other methods of refining, for the removal of important lubricating parts of the crude oil. He thought it was possible that work had already been done on the effects, for example, of various fractions of wax sweatings, but, if not, regarded it as a likely fruitful field for investigation.

Dr. Bruno Engel, referring to the fact that the pour point obtained by dichlorethane dewaxing is lower than the dewaxing temperature, said

that also when dewaxing is carried out according to the analytical methyl ethyl ketone method at — 15° C., a filtrate may be obtained, the pour point of which is lower, *e.g.*, between — 16° and — 20° C. The precipitating properties of the solvents in question are very strong, and further, due to their selective effect, unsaturated and/or aromatic substances are left in the dewaxed oil, lowering its pour point.

MR. C. G. VERVER, replying to one of the President's questions, said that the general rule was that pour-point depressors or wax conditioners were removed with the wax cake owing to the fact that they were precipitated on its surface. However, as it was not a chemical reaction, but an adsorption effect, there was always a definite equilibrium. If the pour point and the amount of, say, a certain pyrogenic dope were plotted on a graph, it was found that the pour point would remain at a certain level, the level being that obtained on the filtrate where no dope was used. Theoretically, at a certain point one would, of course, expect a sharp drop, but actually there was a gradual drop and then a very sudden drop occurring approximately at the point where the wax was saturated with the dope and where the saturation limit had definitely been exceeded.

With regard to the natural occurrence of dopes, it would be seen from their paper that so far the experiments that he and his colleagues had carried out had been done only on distillates, but substances of the dope type had a considerable action and did occur naturally in residual oils. (He thought he had better not discuss residual oils on the present occasion.) Some time ago a paper had been published in the *Journal of the Institution of Petroleum Technologists* entitled "Cold Test for Fuels," by Messrs. Moerbeek and van Beest,* in which a very similar explanation was put forward. He would like, however, to direct attention to the fact that even distillates might contain traces of dopes, and that very often rather misleading results had been obtained and rather surprising claims put forward for new dewaxing solvents by reason of the fact, firstly, that small traces of dopes occurred in distillates, and, secondly, that when a rather high boiling solvent was removed, the small amount of cracking which took place might be just sufficient to lower the pour point by about 5° or 6° C. and give rather upsetting results.

There was one question that he would like to ask on the paper by Messrs. Ba Thi, Hunter and Nash. In their diagrams the authors gave the tie-line as being a straight line drawn through the wax apex. The point representing the composition of the cake, a mixture of filtrate and wax, was taken to be somewhere on this straight line. This assumed that the proportion of oil to solvent in the liquid retained in the wax cake and in the filtrate was the same. As far as he was aware, the authors had worked only with a mixture of somewhat hard crystalline wax in a blue oil. He had not the figures with him, but there were clear indications that a wax of what he called an oil-retaining character had a definite preference for oil rather than solvent; in other words, the point representing cake composition would not be in the tie-line passing through the wax apex.

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* *J.I.P.T.*, 1935, **21**, 155–168.

Mr. Ba Thi, replying to Mr. Verver, said it was assumed that the wax was pure wax. When he and his collaborators wrote their paper, they had not seen the paper by Messrs. Kolvoort, Moser and Verver, but when they saw that paper, they noticed the point which Mr. Verver had just raised. If the residue of the wax, when it had been filtered, contained a different proportion of oil to solvent than the filtrate, then the point representing cake composition would not be on the tie-line. Provided the oil content of the solvent-free wax cake was determined experimentally, this would not affect the computations for the pour point and yield of dewaxed oil and the yield of solvent-free cake.

Mr. J. W. Hyde said that with regard to the photomicrographs shown in Fig. 3 in the paper by Messrs. Kolvoort, Moser and Verver, illustrating the effect of an active body on the crystalline structure of wax precipitated from medicinal oil solution, he should like to ask whether the effect shown might not be due to the increase in viscosity caused by the addition of aluminium stearate. This increase in viscosity would restrict the orientation of the crystal nuclei and microlites, thus preventing the formation of the large crystal plates which occur when no aluminium stearate is present. In this connection it would be of interest to know the percentage of " pyrogenic dope " added to the medicinal oil and its effect on the viscosity at the crystallization temperature.

Mr. C. G. Verver replied that the photographs in Fig. 3 had been taken in a mixture of an oil and a wax, but almost identical results were shown if one worked with a mixture of an oil, a wax and a diluent, such as benzole acetone or some other solvent of that kind. In such conditions the increase in viscosity was very small, and he did not think that the increase in viscosity alone could explain the phenomenon which occurred.

The amount of " pyrogenic dope " added to the mixture of wax and oil was about $\frac{1}{2}$ per cent.

Mr. E. C. H. Kolvoort said he had carried out some filtration experiments with the mixture of oil and wax used in the case of Fig. 3 of the paper, and he found that the filtration rate was greater when the crystals were of small size. The flat crystals blocked the pores of the filter plate, and so decreased the rate of filtration.

Mr. C. R. Scott-Harley said he could confirm Mr. Kolvoort's statement with regard to the size of the crystals in filtering pressable wax distillates. Some time ago he had carried out a series of experiments in filter-pressing ordinary wax distillate from which it was quite clear that the presence of large plate crystals was not conducive to a rapid filtration rate. Taking a given mixture and breaking up the crystals by heat-treatment or by a special method of cooling and making those crystals smaller in size, as seen microscopically under crossed nicols, he found that the filtration rate was at least twice what it had been before.

Another point of interest in connection with this matter, which was a little surprising, was that when filter-pressing a waxy distillate at 78° F., the normal first stage temperature, for these particular oils, one got a

certain rate of filtration, and, taking the blue oil from the above pressing and cooling it down further to 56° F., one found that whilst the viscosity of the oil was appreciably increased, the rate of filtration was not less, as one would expect, but greater—perhaps two or three times greater—than in the first stage. Again, when cooling this blue oil still further to 39° F., the filtration rate was found to be almost double that of the first stage pressing at 78° F., wherein the crystals are relatively large plates. Hence, not only the size but also the nature and concentration of the crystals have a very great influence on the filtration rate.

Mr. Verver and his colleagues had suggested in their paper that there was evidence to show the presence of branched-chain hydrocarbons in the wax fractions, and he would like to know whether they could indicate, even approximately, the relative proportions of normal paraffins and the other types of hydrocarbons in the wax of any contrasting crude oils, such as the Roumanian, the Borneo and the Java? It would be of interest to compare such data with the recent estimates that the wax in Japanese shale oil consists of normal and *iso*-paraffins in the proportion of 4 to 1. Finally, he would like to know whether the authors could supply any information of the latent heats of the branched-chain hydrocarbons?

Mr. C. G. Verver said he could not reply to Mr. Scott-Harley's question from personal experience, but he had recently been fortunate enough to be able to pass on samples of two waxes, one from Roumanian and one from Java oil, of the same molecular weight, to Professor Waterman of Delft. It was well known that Professor Waterman used a method of ring analysis, by which he gave the average composition of mineral oils in terms of aromatic rings, naphthenic rings and saturated chains, but recently he had been working on another method, described in a paper presented at the World Petroleum Congress in Paris, in which he developed an expression for the degree of ramification or branching in a molecule. He did that by means of Sugden's specific parachor. Professor Waterman himself was not yet prepared to express an opinion as to the absolute accuracy of the method, but he certainly had very definite indications that he could arrive at an approximate number of branchings per molecule for a given oil. With regard to the samples of Roumanian and Java wax which he had sent to Professor Waterman, Professor Waterman had sent him a report on them just before he left Holland to attend the present meeting, and the result was rather curious—namely, that the Java wax had no branchings and the Roumanian wax had four branchings per molecule.

Mr. Belchetz asked whether the feathery structures illustrated in the paper by Messrs. Kolvoort, Moser and Verver were characteristic of all waxy distillates, or only of those which crystallized out in plate formation. He had done some work on a distillate the crystals of which tended to be in needle form, and in that case the effect of pyrogenic dopes and soaps seemed to be to distort the shape of the crystal into a round ball. If a solution was made of the dewaxing solvent and the distillate and it was chilled down to the dewaxing temperature in the absence of a dope, then the needle crystals which came out seemed to interlock and

occlude a good deal of solvent and oil, rendering it extremely difficult to filter and wash the cake. As soon as a dope was introduced, the shape of the crystals altered, and, when viewed under the microscope, they had a spherical appearance. The viscosity of the dewaxed mix was then greatly diminished.

He would therefore like to know whether the effect of the dope was to form the feathery crystals shown in the paper, as his own experience had been that its effect was to form " ball-like " crystals.

Mr. E. C. H. Kolvoort said the paraffin wax which he and his colleagues investigated was a very narrow distillate cut from paraffin wax of a normal straight-chain type, and that type crystallized without dope in thin plates. The action of wax conditioners was to diminish the size of the plates, to curve them somewhat and to form feathers, as shown in the photograph in the paper. When paraffin waxes of a less pure type were used, then on the addition of a dope, aggregates of a spherulitic form were produced.

He thought the answer to Mr. Belchetz' question was that the paraffin wax used was of a less pure type than that used by himself and his collaborators.

Mr. C. G. Verver said he thought the whole question turned on whether oil was adsorbed on the surface of the wax or not, and that the form in which the wax came out was probably more or less incidental to the question.

Mr. J. W. Hyde. With reference to the spherulitic structure suggested for the " ball-like " crystals, has Mr. Verver observed the presence of spherulitic structure in wax crystals under the microscope?

Mr. E. C. H. Kolvoort replied that there was such evidence. One saw a black cross, which was typical of spherulites; it was caused by the vibration of the polarized rays.

Mr. F. E. A. Thompson said there was a considerable difference between the materials used by the authors of the first paper, and the materials used by the authors of the subsequent papers, or, for that matter, the materials used in any of the modern solvent dewaxing processes. The Anglo-Iranian blue oil was a relatively light oil which was easily pressable, whereas the newer solvent dewaxing processes were all concerned with removal of wax from non-pressable oils of higher boiling range in which the wax was of a much less well-defined character. The 106–108° F. melting-point wax used in the first paper represented only a 10 per cent. fraction of the oil-free wax removed by cold pressing of the Anglo-Iranian blue oil. Moreover, during treatment of this crude wax any natural pour-point depressor or modifier was removed in the sweating, so that the authors of the first paper were obviously working under rather artificial conditions.

With regard to the second paper by Dr. Engel, he wished to say how necessary he thought it was that more complete analytical data should be given on the dewaxed oils, and not only pour point: for example, Dr.

Engel had stated that when dewaxing an oil with ethylene dichloride in the presence of precipitants, he could obtain lower pour-point oil and higher yield by dewaxing at a higher temperature than he could at a lower temperature. It was, however, common experience that on dewaxing oils with a mixed solvent of this type, certain solvent compositions readily resulted in phase separation at lower temperatures, giving results similar to those experienced by Dr. Engel. Examination of the dewaxed oils, however, invariably showed the effect of this phase separation at lower temperatures by a noticeable decrease in the viscosity index of the "dewaxed oil" despite the higher pour point. For example, the well-known blend of acetone–benzole (35–65 per cent. by volume) frequently results in precipitation of high-grade lubricating oil at low temperatures, together with the wax, giving in effect a dewaxed extract which may have increased pour point due to high viscosity at low temperature. By reducing the proportion of precipitant or by modifying the solvent present, *e.g.* employing benzole–toluene mixtures, this precipitating effect may be avoided. The following figures are illustrative :—

| | S.G. at 60° F. | S.G. at 140° F. | Viscosity (stokes) at | | | V.I. | Pour Pt. |
|---|---|---|---|---|---|---|---|
| | | | 100° F. | 140° F. | 200° F. | | |
| Waxy Stock . | 0·898 * | 0·898 | 5·10 * | 0·904 | 0·248 | 87 | — |
| Dewaxed Oil : | | | | | | | |
| "A" . . | 0·9588 | — | 10·67 | — | 0·415 | 40 | +20 |
| "B" . . | 0·9425 | — | 5·71 | — | 0·312 | 60 | 0 |

* Estimated.

Mr. W. N. Hoyte, referring to Fig. 1 of the paper by Messrs. Kolvoort, Moser and Verver, asked whether any data could be given as to the boiling points of the Roumanian and Java oils dealt with in that figure. He thought that Fraction 10 of the Roumanian oil, which was the one just before the Roumanian oil left the curve for normal paraffin hydrocarbons, and Fraction 23 of the Java oil, would show the limits of filterability of the oils.

Mr. C. G. Verver said he had not any data on the actual boiling points, but he thought he could agree that probably, if one was dewaxing without a solvent, Fraction 10 would approximately correspond to the limit of filterability of the Roumanian oil, and that probably any fractions added to the Java oil above Fraction 23 would spoil its filterability. He thought the points where the curve departed from the normal hydrocarbon line more or less corresponded to the limits at which an oil could be filtered without a diluent. That was rather a rash statement, but it more or less corresponded to what one found in practice.

Dr. Bruno Engel asked whether Mr. Verver and his colleagues had carried out any analyses of the C : H ratio in the waxes obtained in their dewaxing tests. There are some kinds of wax the formula of which is $C_nH_{2n} + 1{\cdot}85$ instead of the theoretical paraffin constitution $C_nH_{2n+2}$.

Perhaps some of the so-called *iso*-paraffins may be such compounds with lower hydrogen content, and may have a detrimental effect on wax crystallization, in the same way as resins and other polymers.

Referring to Mr. Verver's investigations on the reaction of *iso*-paraffins Dr. Engel asked if he had tried to separate normal and *iso*-paraffins by distillation in the cathode-ray vacuum or by treatment with antimony pentachloride.

MR. C. G. VERVER said that he and his colleagues had not actually carried out any elementary analyses, but it must logically follow that if an oil contained adsorbed oil the C:H ratio would vary, because oil definitely contained naphthenic rings which were lower in hydrogen content.

The authors of the fourth paper, Messrs. Pokorny and Stratford, were not present at the meeting, but there was one point he would like to raise on their paper—namely, that it would be an advantage if comparative data were given therein. He and his colleagues in their laboratory had worked with certain homologues as dewaxing diluents. For instance, taking the case of the organic ester series, they found that if they passed from, say, methyl formate to amyl formate—in other words, from a more polar to a less polar solvent—it corresponded to the fact that one had to add less of the solubility-promoting solvent, and he wondered whether the same applied to methyl *n*-butyl ketone, whether in fact methyl *n*-butyl ketone would not simply be equivalent to acetone mixed with a certain amount of diluent. It would be very interesting to have some light thrown on that subject.

There was one definite disadvantage in having a single solvent, in that if one had a pair one could always adjust the solvent to suit the oil. An oil of an aromatic type required a more polar solvent than an oil of a paraffinic type.

On the motion of the President, a hearty vote of thanks was accorded to the authors of the papers, and the meeting then terminated.

# MARINE DRILLING.*

By A. J. Ruthven-Murray, M.A., B.Sc. (Member).

Many years have passed since derricks were first erected over water in different parts of the world to drill in search of oil, underlying swamp lands, canals, lake bottoms and sea beds; it was therefore gratifying to see that the Government of Trinidad published last June a notice stating that they were prepared to receive applications for the grant of exploration licences in connection with oil concessions over marine areas in the territorial waters of the Colony.

It is a long time since several of the Trinidad oil companies first applied for marine concessions, and these have patiently looked forward to the granting of marine licences. Some of these companies have even acquired both the surface and mineral rights for a considerable depth back from the shore so as to create a valuable sphere of influence. This has enabled them to obtain information as to the definite trend of structures underlying the sea.

The notice recently issued by Government has stimulated much interest as to the most economic method of development under the varying conditions existent around the coast of Trinidad.

It will be appreciated that the difficulties to be contended with in sub-marine drilling are many; but in particular these comprise the following :—

(*a*) Special foundations for carrying the derrick and drilling machinery, and also for the boilers or other means of power.

(*b*) Floating equipment for transporting heavy material to and from the wells.

(*c*) The construction of jetties—sometimes in areas subject to severe ground swells—for embarking and disembarking equipment and personnel.

(*d*) The transport of fresh water, fuel oil, gas and mud to the well and crude oil from the well when brought into production.

The methods so far adopted for sub-aqueous drilling have varied considerably from place to place, not only in the United States of America, but also in other countries. In California, where oilfields have been found to extend under the Pacific Ocean, extensive drilling operations have been in progress for many years, principally along the Santa Barbara Channel, and especially at Elwood, where an excellent production has been obtained from wells drilled to 3400 ft. below the sea; some of these wells have produced over two million barrels.

Development at Elwood has been from piers built out from the shore.

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* Paper read at a General Meeting of the Trinidad Branch held at the Apex Club, Fyzabad, on 24th February, 1937, Commander H. V. Lavington, R.N., in the Chair.

As each well was drilled, the pier was extended ocean-wards to the next location; some of these piers exceed 2000 ft. in length and carry half-a-dozen wells spaced at regular intervals of 300 ft., the furthest having been drilled in water more than 50 ft. in depth. This form of pier construction naturally becomes increasingly expensive as extension proceeds into deeper water; the cost varying from $35,000 to $60,000 for a pier extension and well foundation. Some would consider this road connection between well and shore to be a distinct advantage over the transhipment of material from truck to boat; but excepting those locations where the sea is rough, such advantage is questionable, as will be seen later in connection with the handling of material in Lake Maracaibo, Venezuela.

As drilling proceeded into deeper water and upon a structure where the initial yield of oil was declining, it became of increasing importance to cut down the expense of building parallel piers out from shore with continual extensions and single foundations. This was accomplished by the introduction of " Controlled Directional Drilling " from a number of derrick foundations all built side by side together as a unit and located approximately 2000 ft. out from the beach, with a connecting roadway to the shore built on piles. This compound foundation unit is constructed in 40 ft. of water by employing twelve caissons and five cellars, the former being arranged in two rows of six and spaced 24 ft. apart in both dimensions. By this arrangement any running combination of four caissons in the two rows forms a square to support the four derrick corners, and so provides foundations for five positions of the derrick, which, upon completion of work at one location, is skidded over to the next. Seven wells have been drilled from a five-unit foundation : this was accomplished by drilling two wells in each of the end cellars located to shore-ward and ocean-ward, respectively. Two 26-inch conductors placed 2 ft. apart were driven vertically in the first and fifth cellars, the derrick being skidded over this amount when drilling the second well. Although it is possible to start a well with deviation from the surface, this is not usually done. The programme carried out by one of the larger Companies at Elwood is to drill a 21-in. hole vertically to 400 ft. where a 16-in. surface string is cemented. A 15-in. hole is then carried on down vertically to 800 ft., where the offset is commenced, a large hole here being reamed to prevent binding of the drill string. Special deflecting tools are used to start the deviation, these being one of the many types of whip-stock or knuckle joint : the 15-in. hole is then deviated on down to the top of the oilsand, where 10-in. casing is cemented. Ordinary fish-tail and rock-bits are used in this deflection drilling : to increase inclination, a reamer is used directly above the bit with a 5- or 6-ft. drill collar; when a gradual slant is required, a long drill collar is substituted above the reamer. When the correct direction and angle have been obtained, a bladed reamer is used immediately above the bit and on top of the drill collar. It is, of course, the object of the driller to bottom the hole in the producing sand at a pre-arranged point, so as to obtain uniform spacing from well to well; this being so, the angle of deviation will obviously depend upon the depth of the oilsand and the spacing desired. Holes have been drilled and successfully produced where the deviation reached a maximum of 68°. Where the producing horizon is deep, there seems little reason why the compound foundation unit should not be extended to provide for the drilling of more

than seven wells. Conversely, when shallow, the foundation could be reduced to six caissons, thus providing for two derrick locations and four wells; while the speaker has been informed that four wells have been drilled by deflection to the cardinal points of the compass from an extra large cellar located under one derrick foundation.

In Lake Maracaibo, Venezuela, each well is drilled vertically from an independent and regularly spaced location. The foundations for these derricks consist of a group of three piles driven at each of four corners placed 24 ft. apart: at these corners two piles are driven vertically, and steadied by one batter pile driven at a slight angle. These piles are made of reinforced concrete having a cross section approximating to 16 in. × 16 in. for use in water up to 20 ft. in depth: 24 in. × 24 in. up to 50 ft. and 30 in. × 30 in. up to 70 ft. in depth: the overall length varies up to 130 ft. for use in water up to 52 ft. deep, and will be longer for the locations which it is understood are now being prepared in water up to 70 ft. in depth.

After driving to refusal, these piles are cut off at a height of 10 ft. above water; this is done by compressed air chisels and the oxy-acetylene torch. Upon the top of each group of corner piles is cast a reinforced concrete cap 8 ft. square by 4 ft. deep, from which project large steel foundation bolts to hold down the sub-structure or derrick base.

This sub-structure is made up of heavy I section steel girders in the form of a reinforced square having sides 24 ft. × 24 ft. The side over which the draw-works is positioned and the side opposite are composed of girders having a 36-in. webb; the left- and right-hand side girders have a 20-in. webb, while across the middle and spaced about 4 ft. apart run two girders of 36-in. webb to support the rotary table and to take a part weight of the draw-works and the drill-pipe which is racked in front of the drum. All girders are attached to their adjacent members by heavy steel angle plates riveted together. The drilling engine is carried upon two 36-in. girders 15 ft. in length and about 4 ft. apart. These are attached to the external side of the square base as a continuation of the girders which support the rotary. They are braced back to the corners of the principal girder, and are tied together by a distance piece of 36-in. webb riveted between them below the rear end of the engine.

This solidly constructed base is taken out to the location in one piece and then placed by a floating crane upon the four concrete corner caps. The caps are seldom dead level, and in consequence the steel frame is first blocked up level, when concrete is poured on to each cap and brought up to half the depth of the 36-in. girder; this forms a supporting block 16 in. thick underneath each end of the two 20-in. side girders and minimizes vibration. Upon this heavy sub-structure is erected a 122-ft. derrick with reinforced legs. The derrick floor of wood is laid down on top of the steel girders, and this is usually 15 ft. above lake level.

Motive power is derived from boilers, which at one time were placed upon piles, but are now always carried on one end of a large steel barge 80 ft. long by 40 ft. wide and 7 ft. in depth, which, when drilling, is anchored 6 ft. distant from the derrick piles. This barge is divided into eight main compartments each about 20 ft. × 20 ft. × 7 ft., with a small ninth compartment in the centre which is the mud suction pit, 12 ft. × 16 ft. × 7 ft. Of these eight compartments, four at one end and two at the other are for

water ballast, while the other two near the middle are reserve mud pits connected through a manifold to the two 14 in. × 7¼ in. × 14 in. mud pumps mounted on the deck. The six water-ballast compartments are connected through another manifold to a pump mounted near to the front end of the barge. The main deck is of steel sheet, with inspection manholes to each of the eight compartments. These manholes are examined by the driller each tour, to see that they are screwed down tightly, for if left loose and a wind blows up, the compartments will soon fill with water and the barge founder.

A flatish fuel-oil tank is mounted centrally upon the deck at the derrick end, and over this are the pipe racks covering nearly the whole width of the barge. These racks are covered over solid, with sheet steel as a second deck. As pipe, mud and fuel oil are taken from the barge, so is it trimmed by means of the water-ballast compartments.

The boilers are four in number, and on the latest barges have a H.P. rating of 125, and carry 300 lb. of steam. These are placed at the furthest end of the barge in two pairs, port and starboard, with the two water-feed pumps placed centrally between. The firebox ends of the boilers face to the centre of the barge and are approximately 72 ft. distant from the actual drilling well.

The steam line from the engine is brought along to one of the concrete corner pile caps, from which a flexible pipe connects through a quick break union to the barge; an ordinary rotary drilling hose makes the mud connection from the barge to the derrick stand-pipe. A large flexible rubber hose carries the mud returns from well-head to the barge, where it hangs into a mud receiving tank 6 ft. × 6 ft. × 4 ft., mounted on the end of the main deck under the pipe-rack sub-structure. From near the top of this tank runs a steel ditch to the mud suction pit located in the centre of the barge. Near to the front end of the barge are mounted two double drum-steam-operated winches; these carry four lengths of ⅞-in. or 1-in. casing line, to which are attached four 5000-lb. kedge anchors. The anchor cables are conducted from the winches, so as to go off from the barge around capstans at each of the four corners. These anchors, which are placed 500 ft. distant, hold the barge in position 6 ft. from the derrick. In the event of a high wind getting up, which whips the lake into waves over 6 ft. in height, the steam and mud connections are broken and with tackle on the derrick-side the flexible mud return hose is hauled up. The barge then pulls itself away from the derrick by means of the steam winches and kedge anchors.

The boilers draw their water from the lake; this is potable, but slightly brackish in the dry season.

Casing is brought out to the well on a separate barge and transferred to the boiler/drilling barge.

Lake Maracaibo wells average 4300 ft. deep, but one test went to 8700 ft. The formation in general is easy drilling, one driller having been heard to liken it to drilling through a "snow bank." The wells are usually taken down to about 3200 ft. with water flush drawn directly from the lake, and the returns are discharged therein. Below this depth mud is used. The casing programme usually followed is to cement a 13⅜-in. conductor at just over 300 ft., bringing the cement clear up to lake bottom; but before this conductor is run in, 16-in. casing is threaded over the 13⅜-in. for a

length which will protect the latter from a few feet below lake bottom up to above high-water level : this 16-in. casing is drawn in and welded at its lower end to the 13⅜-in., and the annulus between the two then filled with cement. To handle flow connections, etc., steps come down to a wooden platform 10 ft. below the derrick floor; this platform is 10 ft. × 10 ft. and supported on angle iron dropped from the sub-structure. Neither the surface string nor the Christmas Tree is braced to the derrick foundation; but the wooden platform helps to steady the casing in high waves. The programme is completed with a 6⅝-in. combination cemented string.

Upon the completion of the well, the driller, continuing to run tour, rigs down and puts all light tools into the engine-house ready for removal with the engine and house as one unit by the floating crane. The engine is mounted on steel plate which carries a light angle iron-framed engine-house 24 ft. wide, the whole being held down to the sub-structure by four J bolts, while the engine is tied into the draw-works by two turn buckles. The unitary draw-works are only held down in position by two J bolts; it is thus simple to disconnect and lift off this equipment into the barge; the rotary table likewise. The crane barge is then taken alongside the next location and the drilling machinery placed in position and bolted down, small tools rigged up, travelling-block reeved and the well spudded in within sixteen hours of completing the last one. The rig-builders then strip off the reinforcing from the derrick of the completed well, and the rest remains intact in readiness for production purposes when required.

A 6-in. welded pipe-line, for conveying gas to the boiler/drilling barge and crude oil from the well on completion, is laid on the lake bottom from each location to a central production station. This operation is carried out with a special pipe-laying barge, something like a pipe-layer, with a curved trough on one side, over which the pipe, upon being welded up piece by piece, slides off as the barge is pulled ahead to a kedge anchor using a power-driven winch aboard. Black pipe is used, but this is heavily coated with a bituminous compound, including the joints after welding.

Another system of well foundation is that practised in the Black Bayou field of Louisiana, where the field is composed of swamp lands traversed by canals. Here all phases of development, including drilling, repair work and production servicing, are carried out by means of equipment mounted on barges in somewhat similar manner to that employed in the shallow lake waters of Dog Lake, Lake Barre, and the Cameron Island fields of the Gulf Coast.

This system dispenses with piled or coffer dam foundations, but is applicable only where shallow-water conditions appertain. Simply explained, the scheme comprises a steel drilling barge measuring 100 ft. long by 44 ft. wide by 8 ft. deep, down the centre of which from one end runs a longitudinal slot 8 ft. wide and about 56 ft. long. Upon this barge are mounted the drilling derrick, draw-works, engine, mud-pumps, sumps and pipe racks. The four boilers with feed pumps, fuel-oil tanks and water tanks are carried on a separate barge measuring 75 ft. × 25 ft. × 6 ft. deep, and this is connected to the drilling barge by a series of pontoons carrying a walkway and service lines.

The drilling barge is floated on to the location, and then, by admitting water into the hull through a series of valves or sea-cocks, is sunk, so as to

rest upon the bottom of the canal. When drilling is completed, the mud pumps exhaust the water from inside the hull, which again floats; the barge is then towed off from the well-head, such operation being made possible by virtue of the longitudinal slot.

Before the drilling barge is removed, a few guide piles are driven at the end and along each side of the slot, so that these can act as guides to protect the casing-head and again to centralize the production servicing barge over the well. The hull of the servicing barge is similar in design to the drilling barge, but smaller, being only 60 ft. × 30 ft. × 4 ft., but the longitudinal slot is of the same width. This barge carries a production derrick and hoist, but it is not usually sunk, as its buoyance is sufficient for ordinary production work, such as pulling tubing, rods and swabbing.

In Trinidad it is assumed that there is a possibility of finding oil underlying the sea bed along most of the east and west coasts south of the Northern Range, and again along the south coast. An examination of the Hydrographic Charts show that in the Gulf of Paria nearly all bays, of which there are many, have shallows extending from one to two miles out from shore. By shallows is meant a depth of water not exceeding 12 ft. at "mean low water springs," or 19 ft. at "mean high water springs": the maximum differences between high and low tides being as follows:—

| | |
|---|---|
| Port of Spain Harbour . . . . . | 3·8 ft. |
| San Fernando Harbour . . . . . | 5·0 „ |
| Icacos . . . . . | 7·5 „ |
| Guayaguayare . . . . . | 7·0 „ |

The Gulf of Paria is in the lee of the Island, and is therefore protected against the prevailing winds. These comprise two Trades, one from the south-east of eight month's duration, and the other from the north-east for the balance of four months in the year. The wind velocity of these Trades does not under normal conditions exceed a maximum of 25 m.p.h.; but there are occasions in the hurricane season, which lasts from the 15th of July to the 1st of November, when the wind attains a velocity of 35 m.p.h. from the south-west and causes considerable ground swell in the Gulf. Likewise, the North-East Trades will cause a fair swell in the Gulf, but these swells occur but seldom and are of short duration, not as a rule exceeding six hours.

The east coast on the Atlantic Ocean receives the full force of both prevailing winds, and is composed of three almost straight stretches called the Natura, Cocos and Mayaro Bays: throughout the length of the first two bays the sea breaks heavily near shore and the six-fathom line is approximately one mile out. These remarks apply also to the southern half of the Mayaro Bay, except that deep water is closer in. The northern half of this Bay has many shoals, but, even so, five and six fathoms of water occur very close to shore. All three bays are subject to confused sea and tide rips.

The south coast has many bays by name; these, with few exceptions, are little more than slight crenulations of the coastline and are subject to the South-East Trades for the greater part of the year. Broadly speaking, the four-fathom line varies from a half to one mile out; but it must be remembered that this is the five-fathom line at high tide.

On the south coast, Erin Bay and Guayaguayare Bay are the only two where the three-fathom line is more than one mile off shore.

From the foregoing it will be seen that, with the exception of the Gulf of Paria, sea conditions are not favourable to marine drilling; deep water and roughish seas will have to be contended with; but by employing the right system and equipment, it should be possible to overcome these obstacles.

Substantial reinforced-concrete piles with heavy steel sub-structure, as used in Lake Maracaibo, are to be recommended rather than the use of concrete-filled coffer dams: in the first place, the coffer dam presents greater surface to the waves, so that the overturning moment is increased upon wave impact, while this, combined with the effects of erosion by sand scour, may be a serious factor if the foundation is not taken down deep. The coffer dam would also be much more expensive to construct in the sea than piles made on land and driven by a suitable pile-driver.

Wherever marine drilling is undertaken it will be necessary to build a substantial jetty out from shore so as to be able to embark personnel and load barges with all material beyond the line of breakers. The jetty would also carry pipe-lines for fresh water, fuel or diesel oil and mud, for loading into a service barge provided with tanks for each purpose; unless, of course, pipe-lines were laid to the various locations, and it is doubtful if this would prove economical in the long run, for it would necessarily dispense with a barge, as the tanks could be carried in the hull of a pipe- and casing-barge.

The necessary floating equipment will include a powerful shallow-draught tug and a large crane barge equipped with pile-driver. For each drilling string will be required a boiler-drilling barge of the type used on Lake Maracaibo, together with a couple of servicing barges; other equipment will comprise a few launches and speed-boats for the transport of personnel.

For the drilling of a first well in a marine area distant from a source of gas supply, or in the event of developing a marine field of low gas-oil ratio where there was insufficient gas for boiler fuel, it might be advantageous to employ diesel-electric equipment in place of steam. This would show a saving of at least $50 per day over firing boilers on fuel oil; but the cost of diesel-electric equipment with two 6-cylinder diesel engines of 260 H.P. driving two 125-k.w. d.c. generators with one drilling and two pump motors, two 7¼ in. × 14 in. slush pumps and accessory equipment, would be approximately $68,000, as compared with $18,500 for a steam plant consisting of four 125-H.P. 300-lb. boilers with two feed-water pumps, one 12 in. × 12 in. drilling engine and two 14 in. × 7¼ in. × 14 in. slush pumps.

All pipe-lines between wells and shore would have to be laid on sea bottom so as not to molest water transport.

In the Gulf of Paria it should be possible, by somewhat increasing the freeboard, to use the Louisiana type of drilling barge for wells drilled within the one fathom line, and as this extends out for a full mile, some 400 well locations might be sunk off a three-mile shore line. When using this method the boiler barge would be anchored 6 ft. distant and have a flexible steam connection, as the system of pontoons used in Black Bayou would not be practicable. Beyond the one-fathom line the adoption of reinforced concrete piling should prove the most suitable.

Costs for barge equipment and for piles as used in Lake Maracaibo are not

available; but the following are the costs on barge equipment as used in Louisiana :—

| | |
|---|---|
| Drilling barge 100 ft. × 44 ft. × 8 ft. complete, less drilling equipment, but including a Patent royalty payment of $11,250 . . . . . | $38,750 |
| Boiler barge 75 ft. × 25 ft. × 6 ft. to carry four boilers, but less equipment . . . . . | $7,000 |
| Production servicing barge 60 ft. × 30 ft. × 4 ft. . . | $5,500 |

## *DISCUSSION.*

Mr. M. A. ap. Rhys Pryce congratulated the author on a very interesting paper, and one which was out of the ordinary run.

A question he would like to put to the author was with respect to the drilling barges of the Louisiana and Gulf Coast types, whereby the derrick was mounted on a barge and the barge was sunk. The speaker had no experience of that particular type of marine drilling, but it seemed to him that the sunken barge form of drilling pre-supposed :—

(*a*) a flat bottom;
(*b*) an entire absence of swell and current.

It seemed to him that that type of equipment would be entirely impossible with the slightest swell or even in a mild current, and under these conditions with, say, 4000 ft. or 5000 ft. of pipe in the derrick, the chances were that serious trouble would result. He would very much like the author's opinion on that point, as it appeared to him that the Louisiana type of barge would be necessarily limited in its application to Louisiana conditions, where there was a flat bottom and practically stagnant water.

Mr. L. K. White inquired whether the author could tell them of any source of information as to the nature of the sea bottom round the various coasts he described; that was to say, what the depth of the silt or sand would be before solid bottom was reached to make a foundation. If there was no such information, the speaker presumed that any one interested in marine drilling would have to do a considerable amount of exploratory work in that line before a decision could be reached as to whether pile-driven foundations or barge work would be suitable.

Mr. E. Cooper Scott, in answer to Mr. White's query, stated that from pile-driving work his company had been doing recently to try to find a suitable foundation for a new jetty at Pointe-a-Pierre, it appeared that the bottom off Pointe-a-Pierre was very, very variable. The position of the present jetty, he thought, ran about 15 per cent. sand to colloidal matter, and a 12-in. pile could be driven to refusal in about 16 or 18 ft., but at about a quarter of a mile north of that, in a deep which was formed by the depression to the north of the Pointe-a-Pierre grits, no satisfactory foundation could be found at 50 ft. in the sediments. They drove a flat-bottomed pile 50 ft. into the silt, and it was still going ½ in. on every blow of the pile-driver at that depth.

Another interesting thing was that those conditions had changed slightly since the last pile-driving experiments, which might be due to the fact that an opening into the Guaracara River had been cut and turned the deposition to the north, and had deposited about 3 ft. of sandy silt on top of the silt in that area, and that this was replaced by almost entirely colloidal matter deeper down.

Mr. A. Chadwick inquired, with regard to "Controlled Directional Drilling," whether anyone had any experience of production troubles in such wells where a depth of 800 ft. was reached and then the well went off to a maximum of, say, 60°.

In answer to this query, Mr. Rhys Pryce said that in his experience production troubles in holes up to 15° were negligible. In cases where the deviation was over 20–25°, rod and tubing wear could be expected to be heavy, but could be overcome by rod protectors. As far as production methods other than pumping were concerned, the deviation of holes did not make any difference; it was only in pumping wells that serious trouble arose and then not up to 15°.

Mr. J. L. Harris inquired what views the author held in regard to the accuracy of the naval surveys off the coast and in the Gulf of Paria, where the currents and tides alter very much.

He thought that the permanent value of those surveys was very speculative indeed, and was of the opinion that when somebody was ready to start operations in the Gulf, it might be found that it was necessary to operate at depths different from those expected, after taking the naval surveys into account.

Lt.-Col. the Hon. H. C. B. Hickling said that as far as Mr. Harris' point about the accuracy of the naval surveys was concerned, he thought that the records of the Harbour in Port of Spain showed that the original naval surveys of the harbour checked closely with the results obtained before the harbour works started; no appreciable difference was found.

In regard to drilling barges, the speaker thought that the opportunity should be taken to arrange the mud pumps below deck, so that their suction would work flooded.

Mr. A. F. Castle quoted the author's statement that: "In the event of a high wind getting up, which whips the lake into waves over 6 ft. in height, the steam and mud connections are broken, and with tackle on the derrick-side, the flexible mud return hose is hauled up."

The speaker thought that if drilling conditions were similar to those found in most fields in the Island, the severing of steam and mud connections would undoubtedly lead to trouble at certain times, when it was essential that pipe be kept moving, and circulation maintained.

The Author, replying to the discussion, said that Mr. Rhys Pryce had referred to the Louisiana type of barge and questioned its suitability unless it rested on a flat bottom in water free from swell and mild currents. It could definitely be stated that some bays in the Gulf of Paria had level floors, and

it was probable that this condition was general within the shallow bays of the Gulf. There were currents, and at times ground swells, but the author doubted whether these conditions would cause the suspension of drilling, except for a few hours on rare occasions. He thought this because the basal area of the barge was large, it was flooded and sunk, and therefore became a dead weight heavily loaded sitting on a flat bottom. He could not imagine any small swell such as was customarily encountered in the sheltered bays of the Gulf worrying it at all; more especially so when one remembered that the derrick had a 26-ft. base, and so distributed the weight effectively over the width of the barge.

The author had seen sailing barges which, having been washed up on the beach and one-third full of sand, were absolutely rigid, with high waves breaking over them. The absence of swell and current of course enabled Louisiana operators to use pontoons for supporting their steam line from the boiler barge to the drilling barge; but the slight swell here would be sufficient to make one advocate the use of a boiler barge located close up to the sunken barge with steam connections similar to that employed in Lake Maracaibo.

Mr. Rhys Pryce : It is important that the sunken barge does not move the fraction of an inch.

The Author : It must not; but should a high wind or heavy swell arise, then it would be advisable to run the drill-pipe into the hole, and so decrease the resistance and increase the anchorage from the crown block through the derrick.

Mr. Rhys Pryce : The slightest wobble and your water table is out of true.

The Author said he did not think one would have a wobble when located in shallow water in a sheltered bay with flat bottom.

Mr. Rhys Pryce stated that he saw several derricks blow down within a few hours one night in Lake Maracaibo.

The Author pointed out that the winds across Lake Maracaibo have a much greater velocity than they have in the lee of the land in the Gulf of Paria. Only once had he had the experience of derricks blowing down in Trinidad, and that was during the hurricane of 1933, when as far as he had been able to ascertain, only one steel derrick was blown over; the other derricks were of wood, and many collapsed because they were partly rotten or severely weakened by the ravages of white ant.

Resuming, the author said Mr. White spoke about the nature of the sea bottom around the coast in relation to the driving of piles.

Mr. Cooper-Scott gave his views on what had been found at Pointe-a-Pierre. In Guapo Bay, where the author's Company had carried out pile-driving for a jetty, they had found that 2 in. of penetration could still be obtained with a 12 in. diameter pile when driven with a 1-ton monkey at

20 ft. in depth, the formation being composed of 3 ft. of sand and silt overlying interbedded shales and sands.

Regarding Mr. Londsdale Harris' remarks about the accuracy of surveys and the effects of tides and currents, the author proceeded to explain with the aid of a map the course of the various currents; but added that the officers of H.M. Survey Ship *Challenger* had in their recent surveys found surprisingly little difference between the results of this survey and that carried out in 1869. He agreed with Colonel Hickling about the advisability of making use of flooded suction for one's mud pumps, for this might certainly be taken advantage of, and the placing of the pumps at the lower level would also lower the centre of gravity.

With regard to Mr. Castle's remarks on the question of leaving the derrick at an unfortunate time due to high waves, the author thought this a matter for serious consideration, and especially so here in Trinidad, where high gas pressures obtained and barytes-laden mud had frequently to be used. He thought that one might be well advised to have an under-sea mud line connected from the well to a central mud plant on shore provided with power pumps from which circulation of the well could be maintained.

The author regretted that greater discussion on the subject had not been possible, but appreciated that this was a subject of which they in Trinidad had so far not had experience.

On the CHAIRMAN's proposal, a very hearty vote of thanks was accorded the author for his paper, and the President and Members of the Apex Club for the use of their rooms.

# AUTHOR INDEX.


ABRAHAM, W. E. V., Geological Aspects of Deep-Drilling Problems, 378–387, 388, 390
——, on Mud Fluid for Pressure-Drilling Conditions, 399
ASBURY, W. C. and SHEPARD, DAVID A., Research and Development Activities in the Standard Oil Company (New Jersey) Interests, 192–196, 205–206
ASHWORTH, A. A., A Failure of the Standard Method of Estimating the Bituminous Content when applied to a Naturally Impregnated Limestone, 266–269
——, on Anomalous Results for Soluble Bitumen of Natural Rock Asphalts, 642–643
AULD, S. J. M., at Twenty-fourth Annual General Meeting, 306–308
——, on Dewaxing Processes, 752–753
——, on Research in the Petroleum Industry, 201–202

BANKS, F. R., Some Problems of Modern High-Duty Aero Engines and their Fuels, 63–121, 164–177
BASS, E. L., on Modern High-Duty Aero Engines and their Fuels, 145–147
BA THI, M., STRANG, L. C., HUNTER, T. G., and NASH, A. W., The Principles of Solvent Dewaxing, Part I. Equilibria and Computations for Single Solvent Systems, 226–252
——, HUNTER, T. G., and NASH, A. W., The Principles of Solvent Dewaxing, Part II. Equilibria and Computations for Double Solvent Systems, 707–722
——, on Dewaxing Processes, 755
BAYLISS, J., on Geological Aspects of Deep-Drilling Problems, 388
BEALE, E. S. L., A Table of Specific Gravity Correction Factors for Petroleum Oils, 213–219
——, Extended Vapour-Pressure Chart for Hydrocarbons and Petroleum Products, 311–315
——, on Modern High-Duty Aero Engines and their Fuels, 151–153
——, on Temperature Measurements in Oil Wells, 24
——, on Testing Reflection Seismographs, 37–38
BELCHETZ, —., on Dewaxing Processes, 756–757
BENNION, J. E., at Twenty-fourth Annual General Meeting, 303–304
BOADEN, E., on Deep-Well Drilling, 416–417
BOERLAGE, G. D., Remarks on Research, 207–208
BRADSHAW, E. J., on Geological Aspects of Deep-Drilling Problems, 388, 389–390
BRAILEANU, G., on Deep-Well Drilling, 417
BROOKS, R. L., Forestry in Relation to the Petroleum Industry, 524
BULMAN, G. P., on Modern High-Duty Aero Engines and their Fuels, 139–141
BUTLIN, J. A., on Geological Aspects of Deep-Drilling Problems, 387
——, on Mud Fluid for Pressure-Drilling Conditions, 399

CALINGAERT, G. *See* HERON, S. D.
CALLEYA, —., on Deep-Well Drilling, 418
CARTER, ASHLEY, at Twenty-fourth Annual General Meeting, 299–302, 304–306
CASTLE, A. F., on Marine Drilling, 768
CAWLEY, C. M., The Desulphurization of Oils, 209–212
CHADWICK, A., on Marine Drilling, 768
CHAILLET, J. L., on Deep-Well Drilling, 415–416
CHALK, L. J., on Anomalous Results for Soluble Bitumen of Natural Rock Asphalts, 466–467, 643–644
COATES, J., on Geological Aspects of Deep-Drilling Problems, 388
——, on Mud Fluid for Pressure-Drilling Conditions, 399
COLVILL, G. W., Notes on Deep Wells Drilled in Iran, 408–411
COMINS, D., on Deep-Drilling Problems, 375–376
——, on Temperature Measurements in Oil Wells, 22–23, 24–25
CONSTANTINESCU, M., on Deep-Well Drilling, 418–419
COX, P. T., on Deep-Drilling Problems, 374
COXON, G. H., on Modern High-Duty Aero Engines and their Fuels, 153
CUNNINGHAM CRAIG, E. H., on Research in the Petroleum Industry, 202–203

DABELL, C., on Deep-Drilling Problems, 373, 374
——, on Temperature Measurements in Oil Wells, 23
DALLEY, C., at Twenty-fourth Annual General Meeting, 302–303
DAVIES, G. V., on Research in Relation to the Motor Vehicle, 600
DAVIES, R., The Use of Reversed Refraction Arcs in Seismic Surveying, 31–34
DE BREY, J. H. C., Speech at Nineteenth Annual Dinner, 699–700
DIAKOVA, M. K., LOSOVOY, A. V., and STEPANTZEVA, T. G., Hydrogenation of Some Benzene Hydrocarbons under High Pressure, 459–465
DOCKSEY, P., The Design and Analysis of Fractionating Columns for Complex Mixtures, 316–349
DODDS, E. M., on Modern High-Duty Aero Engines and their Fuels, 149–150
DOLL, H. G. *See* SCHLUMBERGER, M.
DUNSTAN, A. E., on Cancer Research Committee, 204–205
——, on Research in the Petroleum Industry, 197–198
DYKSTRA, F. J. *See* HERON, S. D.

EGLOFF, G., Synthetic Products from Petroleum, 645–668
ELIAS, G., on Deep-Well Drilling, 412–415, 419–421
ELLIS, B. J., on Deep-Drilling Problems, 372–373, 374, 375, 376
——, on Temperature Measurements in Oil Wells, 23
EMLYN, A., at Trinidad Branch Annual Dinner, 60
ENGEL, B., Dewaxing with Heavy Solvents, 723–733
——, on Dewaxing Processes, 753–754, 758
EVANS, E. A., on Research in Relation to the Motor Vehicle, 599–600
EVANS, E. B., The Aniline Points of Hydrocarbons, 220–225
EVANS, J. T., Preparation and Control of Mud Fluid for Pressure-Drilling Conditions, 391–399, 400

FEDDEN, A. H. R., on Modern High-Duty Aero Engines and their Fuels, 160–161
FLETCHER, SIR MURCHISON, Speech at Trinidad Branch Annual Dinner, 57–58
FOGG, A. *See* JAKEMAN, C.
FRAME, W. M., A New Type of Threaded Connection for Oil-Well Casing, 422–425

GARNER, F. H., Research in Relation to the Motor Vehicle—Fuels and Lubricants, 575–593, 600–601

HARRIS, J. L., on Marine Drilling, 768
HATFIELD, W. H., on Modern High-Duty Aero Engines and their Fuels, 164
HEINZE, R., and MARDER, M., The Determination of the Ignitability of Diesel Oils on a Laboratory Scale, 602–615
HENDERSON, J. A. L., on Deep-Drilling Problems, 373, 374
HENRIQUES, H. J. *See* MCKITTRICK, D. S.
HERON, S. D., CALINGAERT, G., and DYKSTRA, F. J., The Electrolytic Cleaning of Exhaust Valves, 135–137
HICKLING, H. C. B., on Marine Drilling, 768
HOLLAND, SIR THOMAS H., Speech at Nineteenth Annual Dinner, 691–693
HOYTE, W. N., on Dewaxing Processes, 758
HUNTER, T. G. *See* BA THI, M.
HYDE, J. W., on Dewaxing Processes, 755, 757

ILLING, V. C., on Exploration by Reflection Seismograph, 52, 53–54
——, on Temperature Measurements in Oil Wells, 20, 24
——, on Use of Reversed Refraction Arcs in Seismic Surveying, 34

JACKSON, J. S., on Research in the Petroleum Industry, 203–204
JAKEMAN, C., and FOGG, A., The Lubrication of Journal Bearings in Oxidizing Conditions, 350–366
JONES, J. H., A Method of Testing Reflection Seismographs, 26–31, 39
JONES, LANCASTER, on Testing Reflection Seismographs, 36–37
——, on Use of Reversed Refraction Arcs in Seismic Surveying, 36
JONES, O. T., on Temperature Measurements in Oil Wells, 21–22
——, on Testing Reflection Seismographs, 37

KEEP, C. E., on Geological Aspects of Deep-Drilling Problems, 387, 388
——, on Mud Fluid for Pressure-Drilling Conditions, 399
KEWLEY, J., at Twenty-fourth Annual General Meeting, 309–310
——, on Research in Relation to the Motor Vehicle, 594–595
KLEIN, F. D., Aircraft Engine Performance with 100 Octane Fuel, 121–135

KOLVOORT, E. C. H., MOSER, F. R., and VERVER, C. G., The Influence of Certain Substances on the Separation of Paraffin Wax from Oil in a Dewaxing Process, 734–745
——, on Dewaxing Processes, 755, 757
KREULEN, D. J. W., The Coefficient of Static Friction of Different Lubricating Oils Measured with the "Redgrove Apparatus," 452–458
——, Contribution to the Knowledge of Physical and Chemical Constants of Gas Oils with Different Cetene Numbers, 253–265
——, on The Ignitability of Diesel Oils on a Laboratory Scale, 703–704

LARKE, SIR W. J., on Research in Relation to the Motor Vehicle, 593
LAVINGTON, H. V., Speech at Trinidad Branch Annual Dinner, 58–59
LEENDERTSE, J. J. *See* WATERMAN, H. I.
LEPPER, G. W., on Deep-Drilling Problems, 370–371
LOSOVOY, A. V. *See* DIAKOVA, M. K.

MARDER, M. *See* HEINZE, R.
MASTERSON, E. C., Speech at Roumanian Branch Tenth Annual Dinner, 270–274
MCGHEE, G. C., on Exploration by Reflection Seismograph, 52–53
——, on Testing Reflection Seismographs, 38–39
MCKITTRICK, D. S., HENRIQUES, H. J., and WOLFF, H. I., Petroleum Wax: Determination, Analysis, and Conclusions about Its Composition, 616–641
MELVILL, F. L., Speech at Trinidad Branch Annual Dinner, 59
METSCH, M., on Deep-Well Drilling, 418
MEYER, –., on Modern High-Duty Aero Engines and their Fuels, 154–155
MILLAR, J. H., on Modern High-Duty Aero Engines and their Fuels, 156
MOERBEEK, B. H., on Modern High-Duty Aero Engines and their Fuels, 163
MOSER, F. R. *See* KOLVOORT, E. C. H.
MÜLLER, J., and NEYMAN-PILAT, E., The Chemical Constitutents of Paraffin-Base Lubricating Oils, 669–687

NASH, A. W. *See* BA THI, M.
——, Speech at Nineteenth Annual Dinner, 693–697
NENITZESCU, C. D., The Present State of Our Knowledge on the Origin of Petroleum, 469–482
NEYMAN-PILAT, E. *See* MÜLLER, J.

OGSTON, A. R., Alcohol Motor Fuels, 506–523
——, on Modern High-Duty Aero Engines and their Fuels, 159–160

PALM, E. C. H. *See* WATERMAN, H. I.
PEREBINOSSOFF, A. A. *See* SCHLUMBERGER, M.
PINEAU, J., Speech at Nineteenth Annual Dinner, 697–698
PLOIX, E., on Modern High-Duty Aero Engines and their Fuels, 156–159
POKORNY, O. S., and STRATFORD, R. K., Methyl Normal-Butyl Ketone as a Dewaxing Solvent, 746–750
POMEROY, L., on Modern High-Duty Aero Engines and their Fuels, 153–154
PYE, D. R., on Modern High-Duty Aero Engines and their Fuels, 138, 141

RAMCHANDANI, J. R., The Adsorption of Bitumens by Road Aggregates, 491–505
RAMSAY, F. R. F., on Modern High-Duty Aero Engines and their Fuels, 161–162
RANKINE, A. E., on Temperature Measurements in Oil Wells, 24
——, on Testing Reflection Seismographs, 35–36
——, on Use of Reversed Refraction Arcs in Seismic Surveying, 34–35
REDGROVE, E. R., on Research in the Petroleum Industry, 202
RHYS PRYCE, M. A. ap., on Marine Drilling 767, 769
RICARDO, H. R., at Twenty-fourth Annual General Meeting, 308–309
ROSAIRE, E. E., Exploration by the Reflection Seismograph in the Gulf Coast of Texas and Louisiana, 40–51, 54–56
RUTHVEN-MURRAY, A. J., Marine Drilling, 760–767, 768–769

SANDERS, J. MCCONNELL, The Microscopical Examination of Crude Petroleum, 525–573
SCHLUMBERGER, M., DOLL, H. G., and PEREBINOSSOFF, A. A., Temperature Measurements in Oil Wells, 1–20, 24, 25

SCOTT, E. C., at Trinidad Branch Annual Dinner, 60
——, on Marine Drilling, 767
SCOTT-HARLEY, C. R., on Dewaxing Processes, 755–756
SHEPARD, DAVID A. *See* ASBURY, W. C.
SOUTHWELL, C. A. P., on Deep-Drilling Problems, 369–370, 377
STEPANTZEVA, T. G. *See* DIAKOVA, M. K.
STRANG, L. C. *See* BA THI, M.
STRATFORD, R. K. *See* POKORNY, O. S.

TAUB, A., on Research in Relation to the Motor Vehicle, 595–599
THOMAS, F. M., on Modern High-Duty Aero Engines and their Fuels, 141–145
THOMPSON, A. BEEBY, on Deep-Drilling Problems, 371–372
——, on Temperature Measurements in Oil Wells, 21
THOMPSON, F. E. A., on Dewaxing Processes, 757–758
THORNYCROFT, O., on Modern High-Duty Aero Engines and their Fuels, 150–151
——, on Research in Relation to the Motor Vehicle, 593–594
THORPE, JOCELYN, on Research in the Petroleum Industry, 198–200
TILITSHEYEV, M. D., on Aniline Points of Hydrocarbons, 642
TIZARD, SIR HENRY T., Speech at Nineteenth Annual Dinner, 688–691

UBBELOHDE, L., The Viscometer with Suspended Level (The Elimination of the Influence of Surface Tension by the Suspended Spheric Level), 427–451
UBBELOHDE, L., Speech at Nineteenth Annual Dinner, 698–699
UNDERWOOD, A. J. V., on Modern High-Duty Aero Engines and their Fuels, 155

VAN OS, W. D., on Modern High-Duty Aero Engines and their Fuels, 163–164
VERMEULEN, J. H., Organization of Research in the Petroleum Industry, 179–191, 205
VERVER, C. G. *See* KOLVOORT, E. C. H.
——, on Dewaxing Processes, 751–752, 754, 755, 756, 757, 758, 759

WATERMAN, H. I., LEENDERTSE, J. J., and PALM, E. C. H., The Activity of Oxygen towards Hydrocarbon Mixtures with a High Molecular Weight, 483–490
WHITE, L. K., on Marine Drilling, 767
WHITE, W. W., on Modern High-Duty Aero Engines and their Fuels, 150
WOOD, H., on Modern High-Duty Aero Engines and their Fuels, 147–149
WILLIAMS, C. G., on Research in Relation to the Motor Vehicle, 600
WILMOTH, L. J., on Deep-Drilling Problems, 373–374
WILSON, G. F., Drilling of a Deep-Pressure Test in India, 401–407
WOLFF, H. I. *See* MCKITTRICK, D. S.

YOUNG, C. R., on Deep-Well Drilling, 418

# SUBJECT INDEX.


Acetylene, synthetic, 650
Adsorption of bitumens by road aggregates, 491–505
Aircraft Engines :
  air-cooling versus liquid, 112–114
  collector rings, 84
  combustion chamber design, 75–78
  corrosion, 94–96
  cylinder head design, 75–78
  developments in, 74
  exhaust collectors, 156–158
    pipes, 84
    valves, electrolytic cleaning, 135–137
  fuel tanks, 96–98
  fuels for, 63–177, 521
  ice prevention, 114
  maximum power production, 101–103
  minimum fuel consumption, 101–103
  modern high-duty, 63–177
  performance with 100 octane fuel, 121–130
  sparking-plugs, 84–94
  valves, 78–84
Aircraft Fuels : 63–177
  ethers, 657
  high-octane, 98–101
  ketones, 658
  knock-rating, 70–74, 163
  leaded, effect on tanks, 96
Alcohol Fuels : 148, 506–523, 658–659
  aviation, 68–69, 521
  blending, 511–514
  calorific value, 512, 517
  corrosive and solvent effects, 514–515
  effect on cylinder wear, 515
    engine efficiency, 516–519
  ethanol, calorific value, 512
  higher alcohols, 519–521
  historical survey, 506–508
  *iso*-propyl, 159, 520–521
  manufacture of, 508–511
  use as anti-detonants, 160
Alcohols :
  blending properties, 659
  calorific values, 520
  synthetic, 658
Alloys for aircraft fuel tanks, 96
Aluminium, organo-metallic alkyl derivatives of, 679–687
Annual Dinner, 688–700
Annual General Meeting, 299–310
Annual Report of Council, 1936, 275–285

Benzene, high-pressure hydrogenation, 459–465
Benzole, blending with alcohol and gasoline, 512–513
Bitumen, Bitumens :
  adsorption by road aggregates, 491–505
  estimation in limestone, 266–269
    with panchrometer, 496
      photobitometer, 494–496
  influence of structure on adsorption, 500
  soluble, in natural rock asphalt, 466–467
Burma Branch Annual Report, 1936, 286–288

Carbon monoxide, use in desulphurization, 209–212
Castor Oil, effect of addition of ethyl fluid to, 365–366
Cathode-Ray Engine Indicator, 151–152
Cetene Number, determination, 257
Corrosion :
  by aviation fuels, 94
    leaded fuel, 96
  inhibitors, 95, 97
  of bearings, 590–591
    engine parts, 164

Dehydrogenation of natural gases, 650
Desulphurization with carbon monoxide, 209–212
Detonation, effect of engine on, 598
Dewaxing : 226–252, 707–759
  chlorinated hydrocarbons as solvents, 723–733
  classification of solvents, 243
  dopes, 741, 742
  methyl *n*-butyl ketone as solvent, 746–750
  methyl ethyl ketone as solvent, 754
  pour-point depressants, 742–745
  recovery of solvent, 749
  separation of paraffin wax from oil, 734–745
  solvent systems, equilibria, 707–722
Dichlorethane, dewaxing solvent, 726, 729, 730
Di*iso*propyl ether, synthetic fuel, 67
Drilling :
  cased holes, temperature measurements in, 12
  cementing problems, 14, 15
  deep, 412–421
    geological aspects, 378–390
    in India, 401–407
      Iran, 408–411
      Roumania, 413
  freezing drill pipe, 412
  heaving shales, 412
  marine, 760–770
  steam power for, 412–421

Drilling Equipment :
casing, threaded connection for, 422–425
drill pipe for deep drilling, 414
Drilling Mud. *See* Mud Fluids.

E.G., 174
corrosion inhibitor, 95–96
manufacture of, 131–135
Engines :
aircraft. *See* Aircraft Engines.
bearing corrosion, 590–591
compression ignition, fuels for, 585
trend in design, 586–587
cylinder wear, 515
internal-combustion, ease of starting, 578, 596
research, 575
vapour lock, 580, 597
oil consumption, 591
Ethers, *iso*-propyl, as motor fuel, 657
Ethylene, polymerization, 679
Extreme Line Casing, 422–425

Forestry in relation to Petroleum Industry, 524
Fuel Oils :
diesel, ignitability of, 602–615, 703–704
ignition quality, 585–586

Gas Oils :
oxidation products, 660
physical and chemical constants, 253–265
Gas Sands :
location of, in drilling, 7, 9
temperature gradient reduction near, 20
Gases :
cracked, polymerization, 666
natural, halogenation, 661
Gasoline :
aviation, 63–177. *See also* Aircraft Fuels.
blending, 66, 522, 523
calorific value, 517
octane rating increase, 656
polymer, 65–66, 646–647, 667
solvent extraction to produce high-octane, 663–664
Geophysical Surveying :
seismic, reversed refraction arcs in, 31–39
seismograph, reflection, 40–56
testing of, 26–31
temperature measurements in wells, 1–25

Holde method of wax determination, 623–624
Hydrocarbons :
aniline points, 220–225, 642
Hydrocarbons :
aromatic, alkylation, 654–655
cyclization, 655–656
extended vapour-pressure chart, 311–315
halogenation, 661–663
oxygen stability, 483–490
pure, properties of, 630–635
Hydrogenation :
hexamethylbenzene, 459–460, 461
pentamethylbenzene, 460–461, 462
propylbenzene, 461, 465
1 : 2 : 4 : 5-tetramethylbenzene, 461, 463
xylenes, 461, 464

India, deep drilling in, 401–407
Iran, deep drilling in, 408–411
Iso-octane :
knocking tests, 66
synthesis, 647–648

Kerosene, oxidation products, 660
Ketones, calorific values, 520
Knock Rating, 70–74, 156, 581–582

Limestone, bituminous content of, 266–269, 642, 643
Louisiana Gulf Coast, exploration by reflection seismograph, 40–56
Lubricants : 587–592
bloom-imparting materials, 666
coefficient of static friction, 452–458
dilution of, 581. 598, 601
extreme pressure, 591–592
" oiliness " agents, 591
paraffin base, chemical constituents, 669–678
performance testing, 582–585
pour-point depressants, 732, 733
sludge formation, 590
sulphur content, 209
synthetic, 648–649
Lubrication of journal bearings, 350–366

McNaught's Oil Test, 701–702
Methyl *n*-butyl ketone as dewaxing solvent, 746–750
Methyl ethyl ketone as dewaxing solvent, 754
Molecular weight, apparatus for determination of, 254
Motor Fuels :
cracked, chemical analysis, 663
ethers, 67, 657–658
high-octane, 657, 658
*iso*-octane, 66
ketones, 658
performance testing, 582–585
research on, 575–601
synthetic, 68
*See also* Aircraft Fuels, Alcohol Fuels, Gasoline.

Mud Fluids :
effect of service conditions, 393–395
loaded, 391, 398
preparation for pressure drilling, 391–400
thixotropy, 397–398
viscosity reduction, 396

Natural Gases, halogenation, 661

Obituary :
Chambrier, Paul de, 705
Garrett, Thomas Richard Henry, 426
Manfield, William Hardy, 574
McKeever, Carlos Bernard, 367–368
Spencer, Theodore, 368
Oil Sands, location in drilling, 7, 9
Olefine, Olefines :
anæsthetic properties, 665–666
growth inducers, 664–665
polymerization, 648–650
Oxygen activity towards hydrocarbon mixtures, 483–490

Paraffin, Paraffins :
alkylation, 652–654
isomerization, 656–657
oxidation, 660
Paraffin Wax :
oxidation products, 661
separation from oil, 734–745
Paraflow, 740
Petrolatum, hydrocarbon types in, 639
Petroleum :
composition of, 472–474
deposits, 474–478
microscopical examination of, 525–573
origin of, 469–482, 525–573
synthetic products from, 645–668
Petroleum Industry :
forestry problems in Trinidad, 524
organization of research in, 179–191, 197–206, 207–208
Petroleum Oils, specific gravity correction factors, 213–219
Petroleum Products, extended vapour-pressure chart, 311–315
Petroleum Wax :
composition of, 628–641
determination of, 616–628
effect of asphalt on, 624
fractional crystallization, 623–627
Phenols, alkylation, 654
Polymerization, 646–650
catalytic process, 647
cracked gases, 666
multiple coil process, 647
unitary thermal process, 646
Pour-point depressants, 740–745

Redwood Medal presentation, 307
Refining of Oil, desulphurization, 209–212
Refinery Plant, fractionating columns, design and analysis of, 316–349
Resins, synthetic, 649
Road Aggregates :
adsorption of bitumen by, 491–505
particle-size determination, 493
Roumania, deep drilling in, 413
Roumanian Branch :
Annual Dinner, 270–274
Annual Report, 297–298

Sell, George, an appreciation, 60
Sligh Oxidation Test, 483–484
Sludge Oil, use as pickling inhibitor, 666
Sludge Values of hydrocarbon oils, 484–490
Solvent Dewaxing. *See* Dewaxing.
Specific Gravity Correction factors, 213–219
Standard Oil Company, New Jersey, research and development in, 192–196
South Wales Branch Annual Report, 295–296

Texas, Gulf Coast, exploration in, 40–56
Trichlorethylene, dewaxing solvent, 732
Trinidad Branch :
Annual Dinner, 57–60
Annual Report, 288–290

Venezuela, Lake Maracaibo, drilling operations, 761–764
Viscometers, suspended level, 427–451

Water Flows, location of, 9–12
Wells :
temperature measurements in, 1–25
thermal equilibrium, 3
evolution, 5